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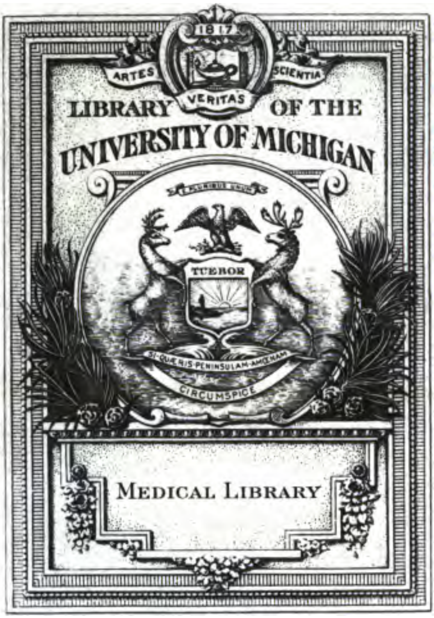
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FIRST BOOK

IN

QUALITATIVE CHEMISTRY.

FIRST BOOK
IN
QUALITATIVE CHEMISTRY.

BY

ALBERT B. PRESCOTT,

Fellow of the Chemical Society of London; Member of the American Chemical
Society; Corresponding Member of the New York Academy of Sciences;
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PREFACE.

THIS little manual has been prepared for certain classes who take a short course in qualitative chemical work, to attain some practical acquaintance with the materials of every-day life, rather than to qualify as analysts. The scope of the work includes a more definite study of bases and acids than is taught in ordinary courses of Experimental Chemistry, and a broader study of chemical characteristics than is provided in the common rudimentary Qualitative Analysis. When a student, with but a few months to devote to chemical laboratory work, should gain, with a little of the training of experimental science, as much insight into chemical action as he can, it is not well that his attention should be all the time directed to a set of chemical peculiarities, prominent only because of their technical use in analysis. The schemes of qualitative analysis furnish admirable avenues by which to reach the chemical study of substances, but the schemes themselves are not especially important to those having no analytical work in view.

The limits of this work, as a First Book, are further explained by the circumstance that it is prepared, primarily, for use under teachers who also employ the author's larger work upon Qualitative Analysis.

Most teachers using this book will direct the work of their classes upon methods of their own. But to any who may be undecided, the author offers the following Schedule, by references to explicit directions in the body of the work. It is advised that, for every two or three hours of laboratory work, an hour be given to recitation in the class-room.

1. A study, or review, of Chemical Notation and the first principles of chemistry, with sufficient practice to be able to write without reference the formulæ of ordinary salts, before commencing laboratory exercises. Paragraphs 1 to 19, inclusive.

2. Laboratory exercise in precipitation of the metals from solutions of their salts by Alkali hydrates, 23 to 26. As to use of reagents, 20 and 21.

3. Practice with the Alkaline Earth metals, in known solutions of their salts, as directed in 58. Require equations, as explained in 47, foot-note, and see that equations

for simple changes of transposition are clearly understood, before going on.

4. Laboratory practice with the Third Group Metals, and group separations, as directed in 125. It would be well to give some chemical problems, upon equations of the work, as introduced in 70, foot-note.

5. Exercises with Second Group metals, and in separation of the groups, 188.

6. Exercises with the Acids (those of primary importance), studying each in a solution of one of its salts, 197 to 314. If time permits, equations for changes of oxidation and reduction, and analytical equations, may now be attended to. The insoluble salts, or precipitations, of each acid and base, to be made thoroughly familiar. Thus, ask for the precipitations possible with ferric sulphate (those common to sodium sulphate and those common to ferric nitrate).

7. Practice in separation and distinction of Acids, in known mixtures containing salts of more than one acid, following the tables, at 317 to 319.

8. Analysis of unknown mixtures of salts, in solid or solution, the mixtures to be so adjusted, and of sufficient variety, that the student cannot at all ascertain the com-

ponents without chemical work. Reports of results received after analysis of every five mixtures.

The work with the bases and acids, in known solutions, should be faithfully and fairly done, even if the time does not admit of taking up analysis.

ALBERT B. PRESCOTT.

UNIVERSITY OF MICHIGAN,
September 5, 1879.

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TABLE OF ATOMIC WEIGHTS

AND

QUANTIVALENCE OF THE ELEMENTS.

(Only the principal degrees of Quantivalence are given.)

Aluminium,	**Al**	IV*	27·3	Mercury,	**Hg**	II†	200·
Antimony,	**Sb**	III, V	122·	Molybdenum,	**Mo**	II, IV*, VI	96·
Arsenic,	**As**	III, V	75·	Nickel,	**Ni**	II, IV*	59·
Barium,	**Ba**	II	137·	Niobium,	**Nb**	V	94·
Bismuth,	**Bi**	III, V	210·	Nitrogen,	**N**	III, V	14·
Boron,	**B**	III	11·	Osmium,	**Os**	II, IV*, VI	198·6
Bromine,	**Br**	I, V	80·	*Oxygen,*	**O**	II	16·
Cadmium,	**Cd**	II	112·	Palladium,	**Pd**	II, IV	106·3
Cæsium,	**Cs**	I	133·	Phosphorus,	**P**	III, V	31·
Calcium,	**Ca**	II	40·	Platinum,	**Pt**	II, IV	197·
Carbon,	**C**	IV	12·	Potassium,	**K**	I	39·04
Cerium,	**Ce**	II	92·	Rhodium,	**Ro**	II, IV*, VI	104·
Chlorine,	**Cl**	I, V	35·5	Rubidium,	**Rb**	I	85·4
Chromium,	**Cr**	IV*, VI	52·4	Ruthenium,	**Ru**	II, IV*, VI	104·
Cobalt,	**Co**	II, IV*	59·	Selenium,	**Se**	II, IV, VI	79·
Copper,	**Cu**	II†	63·3	Silicon,	**Si**	IV	28·
Didymium,	**D**	II	95·	Silver,	**Ag**	I	108·
Erbium,	**E**	II	112·5	Sodium,	**Na**	I	23·
Fluorine,	**F**	I	19·	Strontium,	**Sr**	II	88·
Gallium,				Sulphur,	**S**	II, IV, VI	32·
Glucinum (**Be**),	**G**	II	9·5	Tantalum,	**Ta**	V	182·
Gold,	**Au**	I, III	197·	Tellurium,	**Te**	II, IV, VI	128·
Hydrogen,	**H**	I	1·	Thallium,	**Tl**	I, III	204·
Indium,	**In**	IV*	113·4	Thorium,	**Th**	IV	231·5
Iodine,	**I**	I, V	127·	Tin,	**Sn**	II, IV	118·
Iridium,	**Ir**	II, IV*, VI	198·	Titanium,	**Ti**	II, IV*	50·
Iron,	**Fe**	II, IV*	56·	Tungsten,	**W**	IV, VI	184·
Lanthanum,	**La**	II	92·	Uranium,	**U**	II, IV*	120·
Lead,	**Pb**	II, IV	207·	Vanadium,	**V**	III, V	51·3
Lithium,	**Li**	I	7·	Yttrium,	**Y**	II	61.6
Magnesium,	**Mg**	II	24·	Zinc,	**Zn**	II	65·
Manganese,	**Mn**	II, IV*, VI	55·	Zirconium,	**Zr**	IV	90·

---

* **Pseudo-triads, as (Al_2)^{VI}, (Fe_2)^{VI}, etc.**

† In cuprous compounds, (Cu_2)^{II}. In mercurous compounds, (Hg_2)^{II}.

FIRST BOOK

IN

QUALITATIVE CHEMISTRY.

THE ALPHABET OF CHEMICAL NOTATION.

1. A STUDY of Qualitative Chemistry is a study of the individual components of matter, especially as to their deportment toward each other. Any portion of matter—whether solid, liquid, or gaseous; shapeless, crystalline, or cellular—is made up of one or more *distinct substances.* Thus, a handful of iron filings may contain iron and two different oxides of iron, each of these being a distinct substance, a kind of matter that has the same qualities wherever found. A distinct substance, in this sense, is made up of molecules exactly alike. In the mixture just cited there would be at least three kinds of molecules: those of iron (ferrum), ferrous oxide, and ferric oxide. A mass made up exclusively of molecules of ferric oxide ($\mathbf{Fe_2O_3}$) would be strictly pure ferric oxide.

2. A *molecule* is the smallest possible portion of a distinct substance. It exists free; and it cannot be divided, or chemically united to any other particle of matter, without changing its properties and entering into the formation of one or more other molecules, as least portions of new distinct substances. Thus, any quantity of water is only an assemblage of water molecules; and, if it be strictly pure water, all other molecules are absent.*

3. An *atom* is an indivisible constituent of a molecule. It exists in combination, and its quality is in good part dependent upon its relations to other constituents of its molecule. The atom of chlorine, **Cl**, is a part of the molecule of "common salt," **NaCl**,† and also a part of the molecule of "corrosive sublimate," $\mathbf{HgCl_2}$, ‡ but these two substances are so unlike in properties that the presence of the same kind of atoms in the molecules of each has been discovered only by breaking up these molecules, and obtaining from each the same chlorine atoms, in a new combination.

4. Only sixty-four kinds of atoms have as yet been discovered, and all the matter known in chemistry is made up of combinations of these atoms. In *the elementary bodies*§ the molecules contain atoms of the same kind, in most cases united together in twos. Thus, the molecule of chlorine (free chlorine) is **ClCl**, or $\mathbf{Cl_2}$; and the molecule of iron is **FeFe**, or $\mathbf{Fe_2}$. There are, then, sixty-four known elements.

5. Although the atoms are not found to exist in the free state, their relative weight has been closely determined, and this relative weight, taking the weight of the hydrogen atom (**H**) as the unit, is given as *the atomic weight*. Oxygen (**O**) has the

---

* Water, ice, or steam, each being chemically the same substance, in different physical states. Chemistry is directly concerned only in the formation and character of molecules, not in their aggregation into masses visible to the eye or under the microscope. Chemistry enquires into matter as such, irrespective of the shapes of masses of matter. A snow-crystal is built wholly of water-molecules, but the building together of these molecules to make the crystal is not chemical action. A cell in a plant or animal is built of chemical molecules, of more than one selected kind, but again this building together is not at all chemical action.

† **Na**, sodium; **Cl**, chlorine; sodium chloride.

‡ **Hg**, mercury; **Cl**, chlorine; mercuric chloride.

§ See list of the sixty-four elements, page 13. The term element is applied to a substance not yet decomposed.

atomic weight, 16, and sulphur (**S**), 32. That is, the quantity of oxygen represented by its atom (**O**) is by weight 16 times the quantity of hydrogen represented by its atom (**H**).

6. **Chemical Notation** has for its object to state the composition of molecules. It is the written language of chemistry, common to chemical science all over the world. The alphabet of this language consists of the symbols of the sixty-four elements, each symbol representing an atom. The symbol **O** represents sixteen parts of oxygen, as compared with the one part denoted by **H**, the hydrogen symbol. In practice, the parts may be taken in grains, grams, pounds, or other denominations of absolute weight.

7. The molecule of calcium carbonate is made up of one atom of calcium (**Ca**), one of carbon (**C**), and three atoms of oxygen (**O**); thus, **CaCOOO**, or, more often, $CaCO_3$. The small figures multiply the atom to whose symbol they are appended, as H_2S, a molecule containing two atoms of hydrogen and one atom of sulphur. By use of the parenthesis, collections of atoms are multiplied by small figures affixed, as $Ca(NO_3)_2$, a molecule containing one atom of calcium, two atoms of nitrogen, and six atoms of oxygen. Large figures multiply molecules to whose symbols they are prefixed, as $2CaCO_3$, two molecules of calcium carbonate. Punctuation points limit the effect of prefix figures, as $3MgCO_3.Mg(OH)_2$, three of $MgCO_3$ united with one of $Mg(OH)_2$.

8. The number of atoms must not be confounded with the weight of the atoms as expressed in *parts*. The molecule, H_2S, represents two parts of hydrogen and thirty-two parts* of sulphur the molecule, CO_2, denotes twelve parts of carbon and thirty-two parts of oxygen.

---

* See the Table of Atomic Weights, p. 13.

9. **QUANTIVALENCE.** An atom of chlorine (Cl) unites with one atom of hydrogen (forming HCl); therefore chlorine is styled a monad, or a univalent element, having one bond, and this capacity of combination is denoted thus, Cl'. An atom of oxygen holds two of hydrogen—H_2O—and oxygen is a dyad, or bivalent element, having two bonds, and written O''. In the molecule NH_3, nitrogen holds three hydrogen atoms, it has three bonds, and it is marked N''', a triad, or trivalent element. Carbon is a tetrad, or quadrivalent element, C'''', as shown in the molecule H_4C. Also, in the molecule $C''''O''_2$, the four bonds of the carbon atom hold the four bonds of two oxygen atoms. In the table of the elements (p. 13) is given the number of bonds which each element exercises, in its different conditions. Marks showing the number of bonds, as O'', are convenient to the learner, to keep the quantivalence before the mind, but they are omitted in ordinary chemical notation.*

10. **ACIDS.** An acid may be considered as a salt of hydrogen. It consists of an *Acid Radical*† united with hydrogen which can be exchanged for a metal (this being the formation of a salt). *Oxacids* are those whose radicals contain oxygen, as HNO_3. *Hydracids* are those whose radicals have no oxygen, as HCl; their names begin with *hydr* and end with *ic.* The

---

* Examples for practice—to write compounds of the elements here given, so that, in the molecule written, each element shall have atoms enough to count in all the same number of bonds as the element with which it is combined:

H'	combined	with	Br'
H'	"	"	S''
Na'	"	"	O''
Ca''	"	"	O''
Bi'''	"	"	Cl'
Bi'''	"	"	O''
Sn''''	"	"	O''
Sn''''	"	"	Cl'

† A Radical is a group of atoms, or a single atom, which retains its integrity while transferred from one molecule to another, and is a leading constituent of each.

Anhydride of an oxacid is what remains after removing its H[*] and enough O to form H_2O with the H. Thus, the anhydride of H_2SO_4 is SO_3, and carbonic anhydride is CO_2, carbonic acid being H_2CO_3.

11. Acids whose molecules contain but one atom of hydrogen are termed *monobasic*, as HNO_3 and HCl; those with two atoms of hydrogen in the molecule, *dibasic*, as H_2SO_4 and H_2S; those with three of hydrogen, *tribasic*, as H_3PO_4, etc. As hydrogen is the unit of combining capacity (quantivalence), it follows that the combining capacity, or the number of bonds of the Acid Radical, is expressed by the number of atoms of hydrogen (the basicity) of the acid. We may write HNO_3, with bonds for the acid radical, as $H(NO_3)'$; HCl, as HCl'; H_2SO_4, $H_2(SO_4)''$; and H_3PO_4, $H_3(PO_4)'''$.

12. The following list embraces some of the more important acids. Their notation should be learned:

Notation.	Names of Acids.	Names of Salts.
HCl,	hydrochloric acid, forming	chlorides.
$HClO_3$,	chloric " "	chlorates.[†]
HBr,	hydrobromic " "	bromides.
$HBrO_3$,	bromic " "	bromates.
HI,	hydriodic " "	iodides.
HIO_3,	iodic " "	iodates.
HNO_3,	nitric " "	nitrates.
H_2S,	hydrosulphuric " "	sulphides.
H_2SO_4,	sulphuric " "	sulphates.
H_2SO_3,	sulphurous " "	sulphites.
H_2CO_3,	carbonic " "	carbonates.
H_2CrO_4,	chromic " "	chromates.

---

[*] That is, its *exchangeable* hydrogen. In inorganic acids, all the hydrogen is outside of the radical, and is exchangeable for a metal; in other words, basic hydrogen. But in most organic acids, as $H(C_2H_3O_2)$, the radical itself contains hydrogen.

[†] See paragraph 17.

Notation.	**Names of Acids.**			**Names of Salts.**
H_3PO_4,	phosphoric	acid,	forming	phosphates.
H_3AsO_4,	arsenic	"	"	arseniates.
H_3AsO_3,	arsenious	"	"	arsenites.
H_3FeCy_6,	hydroferricyanic	"	"	ferricyanides.
H_4FeCy_6,	hydroferrocyanic	"	"	ferrocyanides.

The following are classed as organic acids :

$HC_2H_3O_2$,	acetic	acid,	forming	acetates.
$H_2C_2O_4$,	oxalic	"	"	oxalates.

13. SALTS. A salt is formed by substituting a metal for the hydrogen of an acid. And, in this substitution, each bond of the metal displaces one atom of the hydrogen of the acid. Thus (in the formation of normal salts) :

Metals.		**Acids.**		**Salts.**
K'	with	HNO_3	forms	KNO_3, potassium nitrate.
$2K'$	"	H_2SO_4	"	K_2SO_4, potassium sulphate.
$3K'$	"	H_3PO_4	"	K_3PO_4, potassium phosphate.
Ca''	"	H_2SO_4	"	$CaSO_4$, calcium sulphate.
Ca''	"	$2HNO_3$*	"	$Ca(NO_3)_2$, calcium nitrate.
Bi'''	"	$3HNO_3$	"	$Bi(NO_3)_3$, bismuth nitrate.
$3Ca''$	"	$2H_3PO_4$†	"	$Ca_3(PO_4)_2$, calcium phosphate.
$2Bi'''$	"	$3H_2SO_4$	"	$Bi_2(SO_4)_3$, bismuth sulphate.‡

---

* This may be given as follows :

$$Ca'' \text{ with } \left\{\begin{matrix} HNO_3 \\ HNO_3 \end{matrix}\right. \text{ forms } Ca \left\{\begin{matrix} NO_3 \\ NO_3 \end{matrix}\right. \text{ displacing } \left\{\begin{matrix} H \\ H \end{matrix}\right.$$

See paragraph 7.

† $$\left.\begin{matrix} Ca'' \\ Ca'' \\ Ca'' \end{matrix}\right\} + \left.\begin{matrix} H_3PO_4 \\ \\ H_3PO_4 \end{matrix}\right\} = \begin{matrix} Ca''\ PO_4''' \\ Ca'' \\ Ca''\ PO_4''' \end{matrix} + \left.\begin{matrix} HH \\ HH \\ HH \end{matrix}\right\}$$

‡ The student may practise writing salts formed by each of the following metals with each of the following acids :

Sodium, Na'	Hydrochloric	acid,	HCl
Magnesium, Mg''	Carbonic	"	H_2CO_3
Bismuth, Bi'''	Hydrosulphuric	"	H_2S

14. A *normal salt* is one (like all those above) formed from an acid by displacing all its hydrogen by just an equivalent of metal. An *acid salt* is formed by substituting, for a part of the hydrogen of the acid, an equivalent of metal. As follows:

K'	with	H_2SO_4	may form	$KHSO_4$,	an acid sulphate.
K'	"	H_3PO_4	"	KH_2PO_4	" phosphate.
$2K'$	"	H_3PO_4	"	K_2HPO_4	" "
Ca''	"	H_3PO_4	"	$CaHPO_4$	" "
Ca''	"	$2H_3PO_4$	"	$CaH_4(PO_4)_2$	" "

Monobasic acids do not form acid salts.

A *basic salt* is the substitution of a metal in part for the hydrogen of an acid and in part for the half or the whole of the hydrogen of water (H_2O). That is, a basic salt is a compound partly of the nature of a salt and partly of the nature of a hydrate or an oxide (see next paragraph). Thus,

$Bi''' \left\{ \begin{array}{l} O'' \\ (NO_3)' \end{array} \right.$, written $BiONO_3$, an oxy-nitrate of bismuth, is a basic salt.* Again,

$\begin{array}{l} Pb'' \\ Pb'' \\ Pb'' \end{array} \left\{ \begin{array}{l} (OH)'_2 \\ (CO_3)'' \\ (CO_3)'' \end{array} \right.$, written more compactly, $Pb_3(OH)_3(CO_3)_2$, a hydra-carbonate of lead, is termed a basic carbonate of lead.†

A *super-salt* is formed by the combination of a normal salt with the anhydride of its acid (see paragraph 10). Example, potassium super-chromate, $K_2CrO_4 \cdot CrO_3$, or $K_2Cr_2O_7$.

15. **HYDRATES AND OXIDES** of metals. A metallic *hydrate* is formed by substituting a metal for half the hydrogen of water (H_2O), bond for bond. Thus:

K'	with	H_2O	forms	KOH,	potassium hydrate.
Ca''	"	$2H_2O$	"	$Ca(OH)_2$	calcium "
Bi'''	"	$3H_2O$	"	$Bi(OH)_3$,	bismuth "
$(Fe_2)^{vi}$	"	$6H_2O$	"	$Fe_2(OH)_6$,	ferric "

---

* The "subnitrate of bismuth" of the pharmacopœia.

† The ordinary "white lead," used as a paint.

The (OH), left, as above, in combination with metals, as a fragment of the molecule of water, is termed hydroxyl. It is a monad radical.*

A metallic *oxide* is a union of a metal with O''. The formation of an oxide may be considered as the substitution of a metal for all the hydrogen of water (H_2O). The following are examples of oxides:

K'_2O, potassium oxide.
$Ca''O$, calcium "
Bi'''_2O_3, bismuth oxide.
$(Fe_2)^{vi}O_3$, ferric "

16. It will be observed that *the number of bonds of the metal* equals—

The number of bonds of O'' in *oxides*
" " $(OH)'$ in *hydrates.*
" " acid radicals in *normal salts.*

Also in *basic salts,* the bonds of O'' and $(OH)'$ are counted with the bonds of the acid radical, while in *acid salts* the atoms of H' are counted with the bonds of the metal.

The molecules of the most of metallic salts contain *the lowest numbers* of atoms of base and acid compatible with the equality of bonds above stated, but this is not true in all cases. The established formulæ of certain compounds (as Fe_2Cl_6) are not in their lowest terms. The molecular weight (the magnitude of the molecule) is a fact of nature, established if possible from gaseous density and other evidences, and not merely a mode of expression subject to convenience of statement.

17. **NOMENCLATURE.** Among oxacids, those with the termination *ic* contain a greater proportion of oxygen than those ending in *ous*. Thus, H_2SO_4, sulphuric acid; and H_2SO_3, sulphurous acid. If the name of the oxacid ends in *ic*, the names of its salts end in *ate* (as Na_2SO_4, sodium sulphate); if

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* The combinations of hydroxyl are by some chemists termed hydroxides, instead of hydrates.

the termination of the acid is *ous*, that of its salts will be *ite* (as Na_2SO_3, sodium sulphite). The salts of hydracids (paragraph 10) have names ending in *ide* (as Na_2S, sodium sulphide; $CaCl_2$, calcium chloride).

18. The name of the metal receives the termination *ous* when it acts with a lower quantivalence (number of bonds) than another condition of the same metal, the latter being distinguished by the ending *ic*. Thus, $Fe''Cl_2$ is ferrous chloride; Fe_2Cl_6, ferric chloride; Hg_2O, mercurous oxide; HgO, mercuric oxide.*

19. GROUPING OF METALS. In the systematic course of analysis, metals are separated into groups, as follows (omitting those not in common use): †

Group I. *Metals forming chlorides insoluble in water:*

Lead —Pb''—The base of lead salts or plumbic salts.
Silver —Ag' " silver salts or argentic salts.
Mercury—$(Hg_2)''$ ‡ " mercurous salts.

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* The student may practise writing formulæ for the following compounds (uniting, in turn, each base with each acid):

Sodium (Na') Zinc (Zn'') Ferrous (Fe'') Ferric $(Fe_2)^{vi}$	Chloride. Chlorate. Nitrate. Hydrate. Oxide. Sulphide. Sulphite. Sulphate.

† The names, symbols, and number of bonds of these members of each group should be now learned, if the student is not already familiar with them.

‡ In mercurous compounds the atoms have the apparent capacity of monads (Hg'), but it is supposed that they are actual dyads, one of the two bonds of each atom being held by a fellow-atom (Hg'-Hg'). Molecules of mercurous compounds are found to contain an even number of atoms of mercury; therefore, it is said that two atoms have two bonds.

Group II. *Metals whose sulphides are insoluble in water and are not decomposed by dilute acids:*

Mercury —$\mathbf{Hg}''$—The base of mercuric salts.
Copper —$\mathbf{Cu}''$ “ copper salts or cupric salts.
Bismuth —$\mathbf{Bi}'''$ “ bismuth “ or bismuthous salts.
Tin —$\mathbf{Sn}''$ “ stannous “
$\mathbf{Sn}^{IV}$ “ stannic “
Antimony—$\mathbf{Sb}'''$ “ antimonious “
Arsenic —$\mathbf{As}'''$—forming arsenious acid, $\mathbf{H_3AsO_3}$.
$\mathbf{As}^{V}$ “ arsenic “ $\mathbf{H_3AsO_4}$.

Group III. *Metals whose sulphides are insoluble in water but decomposed by dilute acids; also, metals of the earths:*

Zinc —$\mathbf{Zn}''$—the base of zinc salts or zincic salts.
Aluminium—$(\mathbf{Al_2})^{VI}$ “ aluminium salts or aluminic salts.
Iron —$(\mathbf{Fe_2})^{VI}$* “ ferric “
$\mathbf{Fe}''$ “ ferrous “
Manganese—$\mathbf{Mn}''$ “ manganous “
Chromium —$(\mathbf{Cr_2})^{VI}$ “ chromium or chromic “
$\mathbf{Cr}^{VI}$ forming chromic acid, $\mathbf{H_2CrO_4}$.

Group IV. *The metals of the Alkaline Earths:*

Barium —$\mathbf{Ba}''$—the base of barium or baric salts.
Strontium —$\mathbf{Sr}''$ “ strontium or strontic salts.
Calcium —$\mathbf{Ca}''$ “ calcium or calcic “
Magnesium —$\mathbf{Mg}''$ “ magnesium or magnesic salts.

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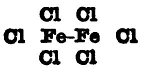
* As the molecules of aluminic and ferric compounds are found always to contain two or some multiple of two atoms of metal, it is stated that two atoms have six bonds $(\mathbf{Fe_2})^{VI}$, instead of giving the atoms as triads, $\mathbf{Fe}'''$. The term *pseudo-triads* is applied to these bases. It is, however, believed that the atoms are actually tetrads, united in pairs by one bond of each ($\mathbf{Fe}'''$-$\mathbf{Fe}'''$). This may be presented, for ferric chloride, as follows:



$$\begin{array}{cccc} & Cl & Cl & \\ Cl & Fe & - Fe & Cl \\ & Cl & Cl & \end{array}$$

Group V. *The bases of the Alkalies:*

Ammonium—$(\mathbf{NH_4})'$—the base of ammonium or ammonic salts.
Potassium —$\mathbf{K}'$—the base of potassium or potassic salts.
Sodium —$\mathbf{Na}'$ " sodium or sodic " *

THE REAGENTS USED IN QUALITATIVE TESTS.

20. The substances most used in making chemical tests are called Reagents, and are supplied upon the table of the student in the laboratory. The greater number of the reagents are kept in the liquid state; a few are used as solids; and sometimes gases are generated when wanted as reagents. Of the liquids, a few, like sulphuric acid, consist of the pure and absolute reagent substance, not diluted, but the greater proportion are substances dissolved in much more than their weight of water. This water, simply a vehicle, and generally not undergoing any chemical change while making tests, is not mentioned at all as one of the substances of a chemical operation. The greater number of tests are made with solutions, and most frequently the distinctive result is the production of a precipitate; that is, the formation of a new substance not soluble in the water present.

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* Examples for practice in writing salts, etc., the combination of each base to be given, in turn, with each acid:

Silver	Chloride	Ammonium	Hydrate
Copper	Nitrate	Magnesium	Chloride
Bismuth	Sulphate	Mercurous	Sulphide
Aluminium	Phosphate	Mercuric	Carbonate
Lead	Hydrate	Sodium	Chloride
Ferrous	Oxide	Bismuth	Bromide
Barium	Nitrate	Antimonious	Sulphide
Calcium	Phosphate	Ferric	Oxalate

21. *In the use of liquid reagents,* they should in most cases be added drop by drop, observing the effect of the first addition. Unless engaged in separations, it is sufficient to take in the test-tube a quarter of an inch in depth of the solution under examination, and to add thereto a few drops of the reagent. Not only economy but accurate work is favored by a very careful and sparing use of materials. Certain of the reagents, however, as specified below, must be used in pretty large proportions. In obtaining precipitates as a means of separation, the precipitation must be completed by adding the reagent gradually, as long as the addition has any effect to increase the precipitate. In adding either acids or alkali hydrates to dissolve precipitates, the dissolving reagent should be used in as small quantity, so as to be as nearly saturated, as possible.

22. **REAGENTS.** These may be mostly classed as Acids, Alkali Hydrates, and Salts. The strength of solutions adopted is that of Fresenius' standard.*

ACIDS.

Sulphuric acid, H_2SO_4. Nearly or quite absolute (*i.e.*, free from water). Specific gravity, 1.843.

Dilute sulphuric acid. A mixture of one part of the absolute acid with five parts of water. Add the acid, gradually and with stirring, in an evaporating-dish, to the water.

Hydrochloric acid, HCl. A water solution, of specific gravity of 1.12; 24 per cent. acid.

Nitric acid, HNO_3. Specific gravity 1.20; 32 per cent. acid.

Nitro-hydrochloric acid, $HNO_3+3HCl=NOCl_2+Cl+2H_2O$. A mixture, made when wanted, of about one part reagent nitric acid to three parts of reagent hydrochloric acid.

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* Reagents should be, for nearly all purposes, chemically pure. Tests as to purity can be made, without specific directions, by those who have had training in analysis, and the beginner must necessarily depend upon others for the selection of reagents.

Hydrosulphuric acid Solution, H_2S. A saturated water solution. Sufficient saturation can be ascertained by the odor, or by blackening of paper wet with lead acetate reagent and held over the mouth of the bottle, or by the bubbles coming outward after shaking the closed bottle and then slowly withdrawing the stopper or the finger held over the mouth. The solution is very dilute, and must be used abundantly. It soon loses strength.

The gas is also applied as a reagent. For this purpose, it is generated in a suitable apparatus, from ferrous sulphide and diluted sulphuric acid (one part absolute acid to about eight parts of water), the gas being conducted into the solution under treatment. $FeS+H_2SO_4=FeSO_4+H_2S$. (For proportions, see 275.)

Acetic acid. $HC_2H_3O_2$. Specific gravity, 1.04; 30 per cent. acid.

Oxalic acid. $H_2C_2O_4$. The crystals ($H_2C_2O_4.2H_2O$) dissolved in ten parts of water.

Tartaric acid. $H_2C_4H_4O_6$. The crystals (anhydrous) dissolved in three parts of water.

Chlorine water. Cl. Water saturated with chlorine. It should bleach wet litmus-paper; but for the iodine test, should be made very dilute.

ALKALI HYDRATES.

Potassium Hydrate, KOH, *Sodium Hydrate*, NaOH. One part of the hydrate dissolved in eight parts of water.

Ammonium Hydrate. NH_4OH or NH_3+H_2O. A water solution of specific gravity, 0.96, and containing about ten per cent. of NH_3, the anhydride.

Calcium Hydrate. $Ca(OH)_2$. A saturated water solution of the hydrate (slaked lime), containing about one part of hydrate to 700 parts of water.

SALTS.

Carbonates.

Potassium Carbonate. K_2CO_3. Solution in five parts of water.

Sodium Carbonate. Na_2CO_3. A solution of one part of the crystallized salt ($Na_2CO_3.10H_2O$) in five parts of water. *The dry salt* is also used.

Ammonium Carbonate. $(NH_4)_2CO_3$. One part of the crystallized acid carbonate, $(NH_4)_4H_2(CO_3)_3$, in four parts of water, with addition of one part of ammonium hydrate.

Sulphides.

Ammonium Sulphide. Normal, $(NH_4)_2S$. Super-sulphide, $(NH_4)_2S_2$. Acid sulphide, NH_4HS. The acid salt and super-salt are yellowish in solution; the normal salt has only a pale greenish tint. The normal salt gradually changes to super-salt in the reagent bottles during use.

Hydrosulphuric Acid or hydrogen sulphide (see Acids).

Phosphates.

Sodium Phosphate. Na_2HPO_4, disodium-hydrogen phosphate, an acid salt. One part of the crystallized salt, $Na_2HPO_4.12H_2O$, in ten parts of water.

Oxalates.

Ammonium Oxalate. $(NH_4)_2C_2O_4$. One part of the crystallized salt, $(NH_4)_2C_2O_4.H_2O$, with 24 parts of water.

Hydrogen Oxalate (see Acids).

Chromates.

Potassium Dichromate. $K_2Cr_2O_7$ or $K_2CrO_4CrO_3$, a super-salt. Solution in ten parts of water.

Sulphates.

Hydrogen Sulphate. H_2SO_4 (see Acids).

Magnesium Sulphate. $MgSO_4$ (see Magnesium Salts).

Ferrous Sulphate. $FeSO_4$ (see Iron Salts).

Chlorides.

Hydrogen Chloride. HCl (see Acids).

Ammonium Chloride (see Ammonium Salts).

Calcium Chloride (see Calcium Salts).

Bromides.

Potassium Bromide. **KBr.** One part dissolved in fifteen parts of water.

Iodides.

Potassium Iodide. **KI.** Solution in 20 parts of water.

Ferrocyanides.

Potassium Ferrocyanide. **K_4FeCy_6.** The crystallized salt ($K_4FeCy_6.3H_2O$) dissolved in 12 parts of water.

Ferricyanides.

Potassium Ferricyanide. **K_3FeCy_6.** Solution in 12 parts of water.

Sulphocyanides.

Potassium Sulphocyanide. **$KCyS$.** Solution in 12 parts of water.

Ammonium Salts.

Ammonium Chloride. **NH_4Cl.** Solution in 8 parts of water.

Magnesium Salts.

Magnesium Sulphate. **$MgSO_4$.** Solution of the crystallized salt ($MgSO_4.7H_2O$) in 10 parts of water.

Calcium Salts.

Calcium Chloride. **$CaCl_2$.** Solution of the crystals ($CaCl_2.6H_2O$) in 8 parts of water.

Calcium Sulphate. **$CaSO_4$.** Saturated solution, containing one part of the salt to about 400 of water.

Calcium Hydrate (see Hydrates).

Barium Salts.

Barium Chloride. **$BaCl_2$.** Solution of the crystallized salt ($BaCl_2.2H_2O$) in 10 parts of water.

Iron Salts.

Ferrous Sulphate. **$FeSO_4$.** Solution of the crystallized salt (green vitriol), $FeSO_4.7H_2O$, in 10 parts of water.

Ferric Chloride. Fe_2Cl_6. One part of the solid salt, $Fe_2Cl_6.6H_2O$, to 15 parts of water.

Copper Salts.

Copper Sulphate. $CuSO_4$. One part of the crystals, $CuSO_4.5H_2O$, to 8 parts of water.

Lead Salts.

Lead Acetate. $Pb(C_2H_3O_2)_2$. One part of the crystals, $Pb(C_2H_3O_2)_2.3H_2O$ (sugar-of-lead), dissolved in 10 parts of water.

Silver Salts.

Silver Nitrate. $AgNO_3$. Solution in 20 parts of water.

Mercury Salts.

Mercuric Chloride. $HgCl_2$. (Corrosive Chloride of Mercury.) One part in 16 parts of water.

Mercurous Nitrate. $Hg_2(NO_3)_2$. One part dissolved in 20 parts of water acidulated with one part of reagent nitric acid.

THE QUALITATIVE CHEMISTRY OF THE METALS.

23. Group V. The Alkali Metals.

In common use.		*Of rare occurrence.*	
Potassium, . . .	**K′**	Lithium,* . . .	**Li′**
Sodium, ...	**Na′**	Rubidium, . . .	**Rb′**
Ammonium, . .	**$(NH_4)'$**	Cæsium, ...	**Cs′**

24. None of the metals of the alkalies are known to common life as free metals. They are too highly combustible to be kept in contact with the air; indeed they oxidize rapidly on contact with water, displacing half the hydrogen and forming hydrates, as follows:

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* Lithium is an alkali metal forming a sparingly soluble carbonate and an insoluble phosphate. Its compounds impart a bright red color to the flame.

$$\mathbf{K + H_2O = KOH + H}$$

Ammonium is the basic radical of ammonium salts, and, as such, has the characteristics of an alkali metal. The water solution of the gas ammonia, $\mathbf{NH_3}$, an anhydride, is supposed from analogy to contain ammonium hydrate, $\mathbf{NH_4OH}$, known as *the volatile alkali.* The other hydrates of this group, **KOH** and **NaOH**, are termed *the non-volatile or fixed alkalies.*

25. *The hydrates and all the important salts of the alkali bases are soluble in water.* These are the only bases whose carbonates, phosphates, and silicates are soluble in water. And the hydrates of all other metals are insoluble in water, except that alkaline-earth hydrates have a slight solubility in water.

From their solubilities, as just stated, it will be observed that *the alkali bases are not precipitated by any ordinary reagents.** They can be changed from one salt to another—as from carbonate to chloride, and from chloride to sulphate—but in each case the new salt, like the old, is one soluble in water, and no precipitate appears.

26. As stated in the preceding paragraph, the hydrates of metals not alkalies are mostly insoluble in water. Now, these insoluble hydrates are precipitated, when an alkali hydrate is added to a solution of a salt of a metal not an alkali. Thus (the precipitate being given in italics):

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* When a dissolved substance is made insoluble, so that it appears as a solid, formed in a liquid mixture, the substance is said to be *precipitated.* If the student will take some reagent solution of silver nitrate, in a test-tube, and add a drop or two of reagent hydrochloric acid, a white precipitate will be observed. The metal silver as a nitrate was soluble in water, but when it changes to chloride of silver it becomes insoluble in water, and appears as a precipitate. Again, add some reagent barium chloride to some reagent magnesium sulphate, and a precipitate is formed, namely: barium sulphate. The chemical change is this:

Barium chloride + magnesium sulphate = *barium sulphate* + magnesium chloride.

Each of the four salts named in this equation is soluble in water, except the one given in italics. (The use of solubility in chemical work is mentioned in paragraph 20.)

Magnesium sulphate + potassium hydrate =*magnesium hydrate* + potassium sulphate.

Rule for Precipitation by Alkali Hydrates: *The Fixed Alkali Hydrates* (**KOH** and **NaOH**) *precipitate all bases not alkali;*[*] *the Volatile Alkali Hydrate* (**NH_4OH**) *precipitates the bases of the first three Groups and Magnesium.*

The precipitates formed are the hydrates of the respective non-alkali metals, except in case of Mercury, Silver, and Antimony (for which see list below).

The precipitates formed are, in certain cases, *soluble in excess* of the alkali hydrate; viz.: excess of the fixed alkali hydrates dissolves the precipitates of **Pb, Sn, Sb, Zn, Al,** and **Cr**; and excess of ammonium hydrate dissolves the precipitates of **Ag, Cu, Zn, Co,** and **Ni.**[†]

The following are the principal **Precipitations by the Alkali Hydrates** (on their addition to solutions of soluble salts of the respective metals):[‡]

Salts Treated.		**Precipitates Formed.**	
Barium	salts—With Fixed Alk.	—**$Ba(OH)_2$**	—Sparingly soluble in water.
Strontium	" — " "	—**$Sr(OH)_2$**	—Sparingly soluble in water.
Calcium	" — " "	—**$Ca(OH)_2$**	—Slightly soluble in water.
Magnesium	" —With all Alk.	—**$Mg(OH)_2$**	—Soluble by ammonium salts.
Zinc	" — " "	—**$Zn(OH)_2$**	—Sol. by excess of fixed or vol. alk.

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[*] The precipitated hydrates of **Ba, Sr,** and **Ca** being sparingly soluble in water, do not appear in dilute solutions.

[†] To illustrate these statements, take some solution of zinc sulphate, and add ammonium hydrate, drop by drop. A precipitate appears, and after further addition disappears. Try silver nitrate solution with ammonium hydrate previously diluted with several parts of water. Try lead acetate solution in the same way with potassium hydrate.

[‡] It would be well for the student to go through the formation of these precipitates, as the first work in the experimental study of the bases.

Salts Treated.		**Precipitates Formed.**	
Aluminium salts	—With all Alk.	—$Al_2(OH)_6$	—Sol. by excess of fixed alkali.
Ferrous	“ — “ “	—$Fe(OH)_2$	
Ferric	“ — “ “	—$Fe_2(OH)_6$	
Manganous	“ — “ “	—$Mn(OH)_2$	
Chromic	“ — “ “	—$Cr_2(OH)_6$	—Sol. in cold fixed alkali.
Copper	“ — “ “	—$Cu(OH)_2$	—Sol. by excess of vol. alkali.
Bismuth	“ — “ “	—$Bi(OH)_3$	
Tin, **Sn''**	“ — “ “	—$Sn(OH)_2$	—Sol. by excess of fixed alkali.
Antimony	“ — “ “	—Sb_2O_3	—Sol. by excess of fixed alkali.
Mercuric	“ —With Fixed Alk.	—HgO	
	“ —With NH_4OH	—NH_2Hg,	Mercurammonium salts.
Mercurous	“ —With Fixed Alk.	—Hg_2O	
	“ —With NH_4OH	—NH_2Hg_2,	Mercurous ammonium salts.
Silver	“ —With all Alk.	—Ag_2O	—Sol. in excess of vol. alkali.
Lead	“ — “ “	—$Pb(OH)_2$	—Sol. in excess of fixed alkali.

27. Solutions of the alkalies (*i.e.*, the alkali hydrates) are *caustic* to the taste and touch, and turn red **litmus-paper** blue. This alkaline effect upon test-paper is given, also, by the carbonates, acid carbonates, phosphates, and some other salts of the alkali bases. The hydrates and normal carbonates of these bases differ from those of other bases in the fact that they are *not decomposed at a red heat.*

28. *Ammonium* is distinguished from all other bases by the easy vaporization of all its compounds, especially of its hydrate (giving off NH_3), see paragraph 38.

Potassium and *Sodium* are found to be alkali bases by not precipitating in any of the groups, and are then distinguished from each other by the colors they give to a non-luminous flame (see, for potassium, paragraph 32; for sodium, 35). In spectral analysis, the alkali metals are very readily identified.

Potassium.[*]

29. *In common use:*

The *Hydrate*, KOH; "Potassa," U. S. P.[†]; "Caustic Potash."

Carbonate, K_2CO_3; three grades in U. S. P., "Impure Carbonate of Potassium," "Carbonate of Potassium," and "Pure Carbonate of Potassium"; older name, "Carbonate of Potash"; "Salt of Tartar," a name used for a grade made formerly, but not at present, by igniting acid tartrate of potassium.

Nitrate, KNO_3. "Nitrate of Potassium," U. S. P.; "Saltpetre"; "Nitre."

Chlorate, $KClO_3$. U. S. P. "Chlorate of Potash."

Iodide, KI. U. S. P. Bromide, KBr. U. S. P.

Acid Tartrate, $KHC_4H_4O_6$. "Bitartrate of Potassium," U. S. P.; "Cream of Tartar."

Potassium compounds are not as abundant as sodium compounds in the mineral kingdom, but they are required much more than sodium compounds by plants and animals, and have an important value as food, in "fertilizers" of agriculture, and in "mineral food" and medicines for man. In the laboratory, sodium compounds may usually be used in place of potassium compounds.

30. Except potassium *Acid Tartrate*, and potassium Platinic Chloride, all ordinary salts of potassium are *soluble* in water. The chlorate is somewhat sparingly soluble in water; the chlorate, sulphate, and carbonate, insoluble in alcohol.

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[*] In *Mineralogy*, Sylvite is potassium chloride; Carnellite is potassium and magnesium chloride; Orthoclase, or "potash feldspar," is a potassium aluminium silicate.

[†] United States Pharmacopœia.

31. **Tartaric acid,** $H_2C_4H_4O_6$, added to concentrated solutions, gives a crystalline precipitate of *potassium acid tartrate,* $KHC_4H_4O_6$, "bitartrate," or "cream of tartar." The precipitation is promoted by adding alcohol, in which it is not at all soluble. The precipitate is not dissolved by acetic acid, but is dissolved by alkali hydrates (as by excess of potassium hydrate), this being due to formation of normal potassium tartrate, $K_2C_4H_4O_6$, "soluble tartar," freely soluble in water.

32. Potassium compounds color **the flame** violet. Try the solid or solution, on a loop of platinum wire, in the non-luminous flame.* Moisten with a drop of hydrochloric acid, as the chloride is more volatile and gives a better flame-color than other salts. The color is seen through **blue glass,** a distinction from sodium, and the means of extinguishing the rich sodium rays which cover the violet when no glass is used.†

Sodium.

33. *In common use :*

Hydrate, **NaOH** ; "Soda," U. S. P. ; "Caustic Soda."

Carbonate, Na_2CO_3 ; crystals, $Na_2CO_3.10H_2O$, the "Carbonate of Sodium," U. S. P. ; anhydrous, the "Dried Carbonate of Sodium," U. S. P. ; crystals in commerce, "Sal Soda." "Bicarbonate of Sodium," U. S. P., is the acid carbonate, $NaHCO_3$. The "saleratus" and "soda" used for baking is the acid carbonate mixed with more or less normal carbonate of sodium.

Chloride, **NaCl**, "common salt."‡

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* If the platinum wire is not clean, and colors the flame, wash with hot water, or moisten with hydrochloric acid and hold in the flame until it ceases to give color.

† Sodium compounds are so generally present in the atmosphere of the laboratory, and they give so strong a color, that the flame of potassium must usually be identified by use of the blue glass to cut off the color of sodium.

‡ In *Mineralogy,* Halite is sodium chloride ; Natrolite, a sodium aluminium silicate ; Albite, a sodium aluminium silicate ; Cryolite, a sodium aluminium fluoride ; "Cubic Nitre" or "Peruvian Nitre," sodium nitrate.

Sulphate, Na_2SO_4. Crystals, $Na_2SO_4.10H_2O$, U. S. P. "Glauber's salt."
Nitrate, $NaNO_3$. "Peruvian Nitre." "Chili Saltpetre."

34. The salts of sodium are *soluble* in water. The metal is not precipitated, in any ordinary combination.

35. Sodium compounds color the **flame** intensely yellow, the color not being visible through blue glass. Traces of sodium compounds so small as to be unimportant impurities in other salts give the yellow flame.

Ammonium.

36. The *Anhydride*, NH_3, ammonia, is gaseous in ordinary conditions. The water solution containing 10 per cent. of this NH_3, is the Reagent, considered a solution of the *Hydrate*, NH_4OH. "Water of Ammonia," U. S. P., has the same strength as the reagent (spec. grav. 0.96). "Stronger Water of Ammonia," U. S. P., represents 26 per cent. of NH_3 (spec. grav. 0.90). There are, in common use, the

Chloride, NH_4Cl, "Chloride of Ammonium" of the U. S. P.; older names being "muriate of ammonia," "hydrochlorate of ammonia," and "sal ammoniac."
Acid Carbonate, $(NH_4)_4H_2(CO_3)_3$, the "Carbonate of Ammonium" of the U. S. P. "Sal Volatile." "Salt of Hartshorn."

37. The salts of ammonium are nearly all *soluble* in water, those least soluble coinciding with the sparingly soluble potassium salts. The acid tartrate may be mistaken for that of potassium.

38. Any salt of ammonium, treated with **potassium hydrate,** or sodium hydrate, or calcium hydrate, and warmed, evolves *ammonia gas*, NH_3, recognized by its odor, and by turning wetted red litmus-paper blue, when a strip is held in the mouth of the test-tube.*

$$NH_4Cl + KOH = KCl + NH_3 + H_2O$$

This test is not hindered by presence of other bases, and in systematic analysis the test for ammonium is made in a portion of the original solution.

39. The hydrate of ammonium solution gives off ammonia at atmospheric temperatures. Ammonium salts are not vaporized at boiling water heat, but, after evaporation of the water of solutions, increase of **heat** (the residue being on platinum foil) easily dissipates the residue, a distinction from other alkali bases.† The only other base whose salts are readily volatilized is mercury (arsenic being classed among the non-metals).

40. Ammonium compounds are capable of oxidation, by strong oxidizing agents, as permanganates, with formation of nitric acid or its salts. This change occurs to some extent in the atmosphere, and in rivers. By reverse change, action of reducing agents, as zinc in potassium hydrate solution, produces ammonia from nitrates.

41. Group IV. The Alkaline Earth Metals.

Barium, **Ba**″	Calcium, **Ca**″
Strontium, **Sr**″ (little used).	Magnesium, **Mg**″

42. Barium, Strontium, and Calcium, oxidize in the air too rapidly to be used in the arts, in the metallic state. Magnesium can be kept in the air, as a free metal, but it burns brilliantly when ignited. In basic power, and in alkalinity of the hydrate, barium is strongest of the four and magnesium the weakest.

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* Avoid touching the paper to the side of the tube, wet with the fixed alkali added.

† Residues of potassium and sodium salts *melt*, when heated on platinum foil, and becoming transparent may be taken as having vaporized.

43. In water **solubility,** the alkaline earth hydrates and sulphates have an orderly gradation as follows:

Hydrates.			**Sulphates.**		
Barium, in ab't	15	p'rts water.	Barium, practically insoluble.		
Strontium	" 60	"	Strontium, in ab't	7000	p'ts w'r.
Calcium,	" 700	"	Calcium,	" 400	"
Magnesium,	" 6000	"	Magnesium,	" 3	"

The *carbonates* and *phosphates* are insoluble in water. Calcium *oxalate* is insoluble, the other oxalates of this group sparingly soluble: barium *chromate* is insoluble, the other chromates more soluble.

44. The Chief Precipitations of Barium, Calcium, and Magnesium.

In solutions of any of their salts soluble in water. Usually, as chlorides, acetates, nitrates (and **Mg**, also, as sulphate).

Solutions causing Precipitation.	**The Precipitates Formed.**		
	Barium.	**Calcium.**	**Magnesium.**
K or **Na** hydrate (free from Carbonate.)	No pre., except in concent. sol.	$Ca(OH)_2$ (Par. 43.)	$Mg(OH)_2$
Ammonium Hydrate.	No precipitate.	No precipitate.	$Mg(OH)_2$, (57 *a*)
K or **Na** or NH_4 Carbonate.	$BaCO_3$	$CaCO_3$	$Mg_4(CO_3)_3(OH)_2$*
Carbonates, with NH_4Cl	$BaCO_3$†	$CaCO_3$†	No precipitate.
Phosphates, Na_2HPO_4	$BaHPO_4$	$CaHPO_4$	$MgHPO_4$‡
Phosphates, Na_3PO_4	$Ba_3(PO_4)_2$	$Ca_3(PO_4)_2$	$Mg_3(PO_4)_2$
Sulphates and H_2SO_4	$BaSO_4$	$CaSO_4$ (Par. 43.)	No precipitate.
Oxalates, $(NH_4)_2C_2O_4$	BaC_2O_4 (not if dilute,	CaC_2O_4	Pre. in concent. sol.
Chromates, $K_2Cr_2O_7$	$BaCrO_4$ (yellow)	Not if dilute.	No precipitate.

* Ammonium Carbonate gives but a partial precipitate with **Mg**.

† Separation from magnesium, used in grouping the bases.

‡ In presence of NH_4OH (and NH_4Cl), the precipitate is $MgNH_4PO_4$.

45. The four alkaline earth metals can be *separated* from other metals, and each other, as follows: The four, from metals of the first three groups, by not precipitating with ammonium sulphide; and from alkali metals, by precipitating with carbonates. Magnesium, from the other three, by not precipitating with carbonates in presence of $\mathbf{NH_4Cl}$; also, by not precipitating with sulphates even in concentrated solutions, and by precipitating with ammonium hydrate. Barium is separated from calcium by precipitating with potassium dichromate; also, by precipitating with calcium sulphate solution. Calcium is distinguished from the other three metals, by first making and filtering out any precipitate by sulphate and then obtaining a precipitate by oxalate.*

Barium.†

46. Barium hydrate is moderately soluble in water (43), the solution being caustic. The chloride is much used as a reagent. The chief *insoluble* salts are the carbonate, sulphate (a good separation from magnesium), chromate (colored, separation from calcium), the phosphate, and iodate.

47. Solutions of barium salts, with **carbonates**, form a precipitate of *barium carbonate*, $\mathbf{BaCO_3}$, white; with **sulphates** (including sulphuric acid), a precipitate of *barium sulphate*,‡ $\mathbf{BaSO_4}$, white (not dissolved by hydrochloric acid); with **chromates**, a precipitate of *barium chromate*, $\mathbf{BaCrO_4}$, yellow; with **phosphates**, a white precipitate, $\mathbf{BaHPO_4}$ from two-thirds metallic phosphate, $Ba_3(PO_4)_2$ from full metallic phosphate solutions.[*] As to Separations, see 45.

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* If ammonium oxalate is added to the dilute solution of calcium sulphate, the result will show how much less soluble is oxalate than sulphate of calcium.

† In *Mineralogy*, Witherite is barium carbonate; and Barite, or "heavy-spar," is barium sulphate.

‡ Precipitated sulphate of barium is much used for a paint, as "baryta white," often forming a part or the whole of articles sold under the names "white lead" and "zinc white." Native barium sulphate is sometimes used for the same purposes.

48. Barium compounds impart to the **flame** a yellowish green color.

Strontium.[†]

49. Strontium compounds mainly agree in *solubility* and in

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[*] The student should write *chemical equations* of all the precipitates, and other chemical changes, as fully as possible, and it is far better to do this while working at the table, or at all events before going on with other substances. The study of the change, made in writing the equation, throws light upon the management of the test and corrects mistakes in manipulating. Taking the precipitates of barium :

$BaCl_2$ with K_2CO_3 gives a precipitate.

Look in the book for the composition of the precipitate; this is never to be assumed upon theory, but always to be learned as a fact, found some time by quantitative analysis and recorded as a part of science. Now, we have :

$$BaCl_2 + K_2CO_3 = BaCO_3 + * \ *$$

Now we consider that if the **Ba** and CO_3 have entered into union in the precipitate, the **Cl** and the **K** have been liberated. We know (or ascertain) that these unite with each other, and unite as **KCl**. As there were two atoms of each of these elements, we complete the equation :

$$BaCl_2 + K_2CO_3 = BaCO_3 + 2KCl$$

In like manner :

$$BaCl_2 + H_2SO_4 = BaSO_4 + 2HCl$$
$$BaCl_2 + K_2CrO_4 = BaCrO_4 + 2KCl$$

Also, by further instruction—

$$BaCl_2 + K_2Cr_2O_7 = BaCrO_4 + 2KCl + CrO_3$$
$$\text{and } CrO_3 + H_2O = H_2CrO_4$$

And for the phosphates—

$$BaCl_2 + Na_2HPO_4 = BaHPO_4 + 2NaCl$$
$$3BaCl_2 + 2Na_3PO_4 = Ba_3(PO_4)_2 + 6NaCl$$

In reference to the last equation, the learner will please observe that each chemical symbol represents, not only a certain *kind* of elemental matter but a certain proportional *quantity* of that matter. The barium in the precipitate must be *equal* to that which was in solution as a chloride. (See paragraph 5.) The truth of the last equation may appear more evident by repeating some of the symbols, instead of using multipliers :

$$\begin{matrix} BaCl_2 \\ BaCl_2 \\ BaCl_2 \end{matrix} + \begin{matrix} Na_3PO_4 \\ \\ Na_3PO_4 \end{matrix} = \left.\begin{matrix} Ba \\ Ba \\ Ba \end{matrix}\right\} \begin{matrix} PO_4 \\ \\ PO_4 \end{matrix} + \begin{matrix} NaCl\ NaCl \\ NaCl\ NaCl \\ NaCl\ NaCl \end{matrix}$$

Three molecules of $BaCl_2$, and two of Na_3PO_4, must be decomposed in order to furnish the atoms for one molecule (the smallest quantity) of the substance $Ba_3(PO_4)_2$.

[†] In *Mineralogy*, Strontianite is strontium carbonate ; and Celestite is strontium sulphate.

precipitations with corresponding barium compounds. As to the hydrate and sulphate, see paragraph 43. The chromate, and iodate, are more soluble than the same salts of barium. The dilute solution of **calcium sulphate**, with strontium salts, forms a thin precipitate after standing five to ten minutes (free hydrochloric acid preventing the precipitation). This slow precipitation distinguishes strontium from calcium.

50. Strontium compounds (with hydrochloric acid, on the platinum wire) color the *flame* crimson (characteristic). Seen through blue glass, the flame appears purple to rose-red. Strontium salts are used to give red light in fire-works.

Calcium.

51. The calcium compounds of most *common use* and occurrence include—

Oxide, **CaO**. Quicklime. "Lime," U. S. P.
Hydrate, **$Ca(OH)_2$**. Slaked Lime. "Hydrate of Lime," B.P.
Carbonate,* **$CaCO_3$**. Limestone. Marble. Chalk.
Sulphate,† **$CaSO_4$**. Gypsum, **$CaSO_4.H_2O$**; this, when partly dehydrated, is "Plaster of Paris."
"*Chlorinated Lime*," U. S. P., "chloride of lime," **$CaCl_2.Ca(ClO)_2$**. See Hypochlorites.

52. The *solubilities* of the hydrate and sulphate are given in paragraph 43. The carbonate, phosphate, and (distinctively) the oxalate are insoluble in water. The chloride is the soluble salt most used in analysis.

53. Calcium salts in solution, with fixed alkali **hydrates** (not ammonium hydrate), give a precipitate of *calcium hydrate*,

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* In *Mineralogy*, Calcite, and Aragonite.

† In *Mineralogy*, Anhydrite is anhydrous calcium sulphate; and Gypsum is hydrous calcium sulphate. Fluorite, or fluor spar, is calcium fluoride.

$Ca(OH)_2$, the same as "slaked lime," soluble in about 700 parts of water (and not appearing in solutions of this dilution). With soluble carbonates, *calcium carbonate*, $CaCO_3$, is precipitated ("precipitated carbonate of calcium," U. S. P., "prepared chalk"), distinguished from the magnesium carbonate by not dissolving in ammonium chloride solution. With **phosphates** a precipitate is obtained, $CaHPO_4$ from dimetallic phosphate; $Ca_3(PO_4)_2$, the phosphate in bone earth, from full metallic phosphate reagents. With **oxalates**, calcium salts form a nearly insoluble precipitate, *calcium oxalate*, CaC_2O_4,* much relied on in the final determination of calcium.† The precipitation is hastened by adding ammonium hydrate. As to separations of calcium, see 45.

54. Compounds of calcium color the **flame** yellowish-red. Calcium carbonate, after ignition, colors moistened red litmus-paper blue. Calcium compounds, when ignited, glow with white light.

Magnesium.

55. *In common use:*

Oxide, **MgO**. "Magnesia," U. S. P.; "Calcined Magnesia."
Basic Carbonate, $Mg_4(CO_3)_3(OH)_2$. "Carbonate of Magnesium," U. S. P.‡

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* Calcium oxalate, or "oxalate of lime," is of much interest in pathological chemistry, as a constituent of the urine, generally in octahedral crystals, found by the microscope. It also forms a vesicular calculus. It is found in numerous plants.

† See note under paragraph 45. Make a mixture of about equal portions of solution of calcium chloride and solution of barium chloride. (Strontium chloride may also be added.) Add a solution of some alkali metal **sulphate**, as K_2SO_4, adding enough to complete the precipitation. Filter out this precipitate, through a paper filter, folded and placed in a funnel. To the filtered liquid, that is, the *filtrate*, add ammonium **oxalate** (and ammonium hydrate): the resulting precipitate contains the calcium (as oxalate) free from barium (and from strontium). See Table, at 59.

‡ In *Mineralogy*, Magnesite is magnesium normal carbonate; Dolomite is calcium magnesium carbonate; Brucite is magnesium hydrate. Talc, steatite, and soapstone are silicates of magnesium and other bases.

Sulphate, $\mathbf{MgSO_4}$. Crystallized, $\mathbf{MgSO_4.7H_2O}$, "Sulphate of Magnesium," U. S. P.; "Epsom salt."

56. The **insoluble** salts mostly obtained as precipitates are the hydrate, and basic carbonate, both distinguished from others in the same group by their solubility in ammonium chloride, and the phosphates, insoluble with ammonium chloride. In solution, the sulphate and chloride are most used.

57. *a.* Magnesium salts in solution, with **fixed alkaline hydrates**, give a precipitate of *magnesium hydrate*, $\mathbf{Mg(OH)_2}$, very slightly soluble in water (see 43). With **ammonium hydrate**, the same precipitate is obtained, while half the magnesium remains in solution as a soluble magnesium-ammonium salt:

$$2MgCl_2 + 2NH_4OH = Mg(OH)_2 + (NH_4Cl)_2MgCl_2$$

An addition of ammonium chloride dissolves all the precipitate:

$$Mg(OH)_2 + 4NH_4Cl = (NH_4Cl)_2MgCl_2 + 2NH_4OH$$

b. With **carbonates**, magnesium salts give a precipitate of *magnesium basic carbonate*, variable, the most common result being $\mathbf{Mg_4(CO_3)_3(OH)_2}$ (three-fourths carbonate and one-fourth hydrate), the "carbonate of magnesia" of the shops. The precipitate is dissolved by ammonium chloride, and by most of the salts of ammonium.

$$4MgSO_4 + 4Na_2SO_4 + H_2O = Mg_4(CO_3)_3(OH)_2 + 4Na_2SO_4 + CO_2$$

c. With **phosphates**, magnesium salts give a precipitate, not dissolved by ammonium chloride, as $\mathbf{MgHPO_4}$, from dimetallic phosphate solutions. If **ammonium hydrate** is added with the phosphate solution, and also ammonium chloride be added to prevent formation of any magnesium hydrate, a slow-forming but complete precipitate is obtained, *magnesium ammonium phosphate*, **$MgNH_4PO_4$**.*

58. *Exercises with the Fourth Group of Metals.*

a. Work with a solution of a salt of each metal, successively, following the text, and the table at paragraph 44, and writing equations for all changes.

b. Try the *separation of calcium from magnesium, by ammonium chloride*, proceeding as follows : Mix solutions of the two salts, as calcium chloride and magnesium chloride. Add ammonium chloride, ammonium hydrate, and ammonium carbonate, adding enough, and waiting a few minutes, to get a complete precipitate (*a*) (evidence of the *calcium*). Filter. The filtrate (filtered liquid) from pre. *a* is now treated with sodium acid phosphate, **Na_2HPO_4**, when a precipitate is obtained (*b*) (evidence of the *magnesium*). See Table, at 59. Do not attempt equations, for changes in mixtures having more than one base.

c. The student would do well now to practise the separation of **Ba**, **Ca**, and **Mg**, from a solution containing their chlorides together, working from Table at 59, and consulting paragraph 45. Write some "Analytical Equations," as directed at *Note d*, 59.

d. Another method of separating **Ba** from **Mg** is by use of a *sulphate*. To mixed chlorides of barium and magnesium, in solution, add a sulphate of an alkali metal (or **H_2SO_4**), and filter out the **$BaSO_4$**. To the filtrate, add ammonium chloride, ammonium hydrate (enough to make the mixture alkaline to test-paper), and then the sodium phosphate, to precipitate **$MgNH_4PO_4$**.

e. Again, from solution of mixed **Ca** and **Mg** chlorides, add ammonium *oxalate*, to precipitate the calcium, and filter, then treating the filtrate with *phosphate*, to show the magnesium.

Of course the addition of phosphate is not a test for magnesium while either of the other alkaline earth metals is present. Further, see par. 300.

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* $MgSO_4 + Na_2HPO_4 = MgHPO_4 + Na_2SO_4$
$MgSO_4 + Na_2HPO_4 + NH_4OH = MgNH_4PO_4 + Na_2SO_4 + H_2O$

59. ANALYSIS OF GROUP IV. For **Ba**, [**Sr**], **Ca**, and **Mg**. (In explanation of Plan, see 45.)

To the solution containing only Groups IV. and V., or the Filtrate from Group III., add **Ammonium Chloride, Ammonium Hydrate,** *and* **Ammonium Carbonate,** *warm for some time, and filter.*

<table>
<tr>
<td colspan="2">Precipitate : $BaCO_3$ [$SrCO_3$], $CaCO_3$.
<i>Dissolve the well-washed precipitate in diluted</i> Acetic Acid (Note <i>a</i>).
Solution : $Ba(C_2H_3O_2)_2$, [$Sr(C_2H_3O_2)_2$], $CaC_2H_3O_2$. [For Sr, Note <i>c.</i>]</td>
<td>Filtrate : $(NH_4)_2Mg$ sol. salt (57 <i>a</i>).
For Magnesium.
<i>To a small portion of the Filtrate, add</i> Sodium Phosphate, Na_2HPO_4, <i>and stir with a glass rod.</i>
A precipitate ($MgNH_4PO_4$) indicates magnesium.
See Table at 44, and the text at 57.</td>
</tr>
<tr>
<td>For Barium.
<i>To a small portion of the solution add</i> Potassium Dichromate.
A precipitate, $BaCrO_4$, yellow, indicates barium.
<i>For confirmation, to another small portion of the solution, add</i> Calcium Sulphate.
An immediate precipitate, $BaSO_4$, indicates barium.
[A precipitate after some minutes indicates strontium, 49. Note <i>c.</i>]
For barium, see Table at 44, and the text at 47.</td>
<td>For Calcium.
<i>To the remainder of the Acetate Solution add</i> Dilute Sulphuric Acid (or K_2SO_4), <i>drop by drop, to complete the precipitate, if any is formed.</i> Filter out and reject this precipitate (so removing Ba and Sr).
<i>To the last Filtrate, add</i> Ammonium Hydrate <i>to alkaline reaction</i> (Note <i>b</i>), <i>then add</i> Ammonium Oxalate.
A precipitate, CaC_2O_4, indicates calcium.
See the Table at 44, and the text at 53.</td>
<td>The remainder of the Filtrate is the material to be tested for Fixed Alkali Metals. RESERVE for work by Table on page 48.</td>
</tr>
</table>

Notes to the Table for Analysis of Group IV.

Note a. *To filter and wash :* A folded filter is placed in the funnel (the edge of the paper trimmed to come below the rim of the funnel), and the filter wetted with distilled water. The precipitate, with the liquid in which it is formed, is poured into the filter, the funnel being adjusted over a small beaker or other receiving vessel. When the liquid has drained away, add a little distilled water, directed in a fine stream, from the wash-bottle, upon the border of the precipitate, When this water has drained away, add again, and wash at least for the third time. Now, *to dissolve the precipitate :* In the first way, *on the filter :* Setting under a clean beaker, add the solvent, diluted if so directed and warm if need be, upon the precipitate, adding no more than necessary. *An excess of the solvent is nearly always a disadvantage to subsequent work*, unless expelled by vaporization with heat. Substituting another receiver, the solvent can be returned to the filter, again and again, till it is nearly saturated with the precipitate. At last, the solution in the paper can be saved by washing it out with one or two small portions of water. *To dissolve the washed precipitate in a test-tube* (better when the solvent acts slowly) : Pierce the point of the filter with a glass rod, and rinse the precipitate from the filter through into a clean test-tube, changing this receiver and rinsing again with the same portion of solvent, if need be, and last rinsing with a few drops of water. The precipitate is now warmed, long enough, in the test-tube, when, if there is any residue, it is filtered out with a new filter.

To concentrate the solution, or to drive off from it an excess of the acid or other solvent, it is best to use a porcelain evaporating dish, over a gentle heat, afterward rinsing the last portion of the concentrated solution from the dish with a few drops of distilled water.

Note b. *In adding to cause an alkaline reaction*, or the reverse, place a slip of litmus-paper in the solution, and add the reagent, drop by drop, till the test-paper changes color.

Note c. *To identify Strontium :* Test a concentrated portion of the Acetate Solution, on a loop of platinum wire, moistened with hydrochloric acid. (See 50.) Again, as another method, remove the barium (if present) by precipitating the Acetate Solution with Dichromate and filtering. Precipitate strontium and calcium, from this filtrate, by ammonium carbonate and hydrate. Dissolve this (filtered) precipitate with hydrochloric acid, and heat the solution in an evaporating dish to expel the excess of acid. Lastly, treat this solution (or, in absence of barium, the original Acetate Solution, concentrated) with solution of Calcium Sulphate. A slow-forming precipitate is evidence of strontium, paragraph 49.

Note d. It is well to practise writing equations for the successive chemical changes of a metal while being separated from other metals. These are sometimes called "Analytical equations" :

(1) $CaCl_2 + (NH_4)_2CO_3 = CaCO_3 + 2NH_4Cl$

(2) $CaCO_3 + 2HC_2H_3O_2 = Ca(C_2H_3O_2)_2 + H_2O + CO_2$

(3) $Ca(C_2H_3O_2)_2 + (NH_4)_2C_2O_4 = CaC_2O_4 + 2NH_4C_2H_3O_2$

60. ANALYSIS OF GROUP V. For NH_4, K, Na, [and Li].

For Ammonium.	**For Potassium.**	**For Sodium.**	**For Lithium.**
Treat a portion of the original material (in solution or solid), in a test-tube, with solution of **potassium** *or* **sodium hydrate,** *or* **solid calcium hydrate,** *at a gentle heat.*	*Test a portion of the filtrate from the first precipitate of Group IV.* (59) *by the flame of Bunsen's burner, using platinum wire* (32).	*Test a portion of the filtrate from the first precipitate* (**RESERVE**) *of Group IV., for the flame color* (35).	*Test another portion of the* **RESERVE** *of Group IV., for the flame color.*
The vapor of ammonia, **NH_3**, the evidence of ammonium compounds, is recognized by its odor, and its effect on moistened red litmus-paper. **See 38.**	A violet flame, *not obscured by the blue glass*, indicates potassium.	Yellow, obscured by blue glass, indicates sodium, the test being obtained from insignificant traces of sodium compounds.	See note under 23.

61. Metals of Group III.

Of Common Occurrence.		Of Rare Occurrence.	
Zinc,	Zn''	Uranium,	Ur'', $(Ur_2)^{v}$
Aluminium,	$(Al_2)^{vi}$	Indium,	$(In_2)^{vi}$, In^{iv}
Iron	Fe'' in ferrous compounds.	Glucinum,	Gl''
	$(Fe_2)^{vi}$ in ferric "	Thorium,	Th^{iv}
Mn	Mn'' in manganous "	Zirconium,	Zr^{iv}
	$(Mn_2)^{vi}$ in manganic "	Cerium,	Ce'', $(Ce_2)^{vi}$
	Mn^{iv} in pyrolusites.	Lanthanum,	La''
	$H_2Mn^{vi}O_4$, manganic acid.	Didymium,	D''
	$H_2Mn_2O_8$, permanganic "	Titanium,	Ti'', $(Ti_2)^{vi}$, Ti^{iv}
Cr	$(Cr_2)^{vi}$ in chromic compounds.		
	$H_2Cr^{vi}O_4$, chromic acid.	Tantalum,	Ta^{v}
Co	Co'' in cobaltous compounds.	Niobium,	Nb^{v}
	$(Co_2)^{vi}$ in cobaltic "	Yttrium,	Yt''
Nickel,	Ni''	Erbium,	E''
		Vanadium,	V''', V^{v}

62. The metals of this group gradually *oxidize* at their surfaces by contact with the air. Their oxides all yield their oxygen to alkali metals. Oxides of iron, zinc, and nickel give up their oxygen to carbon, by ignition at white heat with charcoal, as occurs in the manufacture of these metals. Iron is gradually oxidized from ferrous to ferric combinations by contact with the air.

63. The hydrates and carbonates of third group metals are **insoluble** in water. Their sulphides are insoluble in water (a separation from the fourth and fifth groups), but are not precipitated in presence of dilute acids (the separation from groups I. and II.) Aluminium and Chromium do not form sulphides, being precipitated as hydrates when sulphides are added to their salts; but these hydrates, like the sulphides of the third group, are dissolved by dilute acids and so excluded from the second group.

64. Cobalt, nickel, manganese, and iron give characteristic colors to beads of borax and microcosmic salt, fused on a loop of platinum wire, before the blow-pipe. Iron, cobalt, and nickel, smelted on charcoal, are reduced to compounds attracted by the magnet, but are scarcely at all reduced to the metallic state, before the blow-pipe.

65. Comparison of Third Group Bases.

In solution of any of their salts soluble in water. Usually as sulphates, chlorides, nitrates, acetates.

Solutions added.	**Zinc.**	**Aluminium.**	**Ferricum.**	**Ferrosum.**	**Manganese.**	**Chromium.***
KOH or NaOH in excess.	*Solution* (72).	*Solution* (77).	*Precip.* (94).	*Precip.* (91).	*Precip.* (102).	*Precip.* (109).†
NH_4OH in excess.	*Solution.*	*Precip.*	*Precip.*	*Precip.*	*Precip.*	*Precip.*
NH_4OH (excess) with NH_4Cl‡	*Solution.*	*Precip.*	*Precip.*		*Solution* (102).	*Precip.*
Carbonates. §	*Pr. basic carb.*	*Pr. hydrate.*	*Pr. hydrate.*	*Pr. carbonate.*	*Pr. carbonate.*	*Pr. hydrate.*
Sulphides. §	*Pr. sulphide.*	*Pr. hydrate.*	*Pr. sulph.* (94).	*Pr. sulphide.*	*Pr. sulphide.*	*Pr. hydrate.**
H_2S in acid solution.	*No pre.* (73).	*No pre.*	*Pre. only S.*	*No pre.*	*No pre.*	*Pre. only S.*
Oxidizing agents.				*Ferric co's.*	*Base to acid.*	*Base to acid.*
Reducing agents. ‖			*Ferrous co's.*		*Acid to base.*	*Acid to base.**

* Chromic acid and its salts, with sulphides, in Third Group precip., appear as chromic base (113).

† Excess of the hydrate, not heated, leaves the chromium in solution, precip. on boiling.

‡ This division of the group into two sections (**Al, Fe, Cr**) and (**Zn, Mn, Co, Ni**) is much used in analysis, the iron being first all oxidized to ferricum (67).

§ The pseudo-triads are precipitated as hydrates by carbonates, and, except ferric salts, by sulphides.

‖ Sulphides and **H_2S** are reducing agents.

66. *The plan of separations by Table at par.* 126. Having the third group alone, in solution (as by dissolving the group precipitate with hydrochloric acid), an **excess of fixed alkali hydrate,** with brief boiling (to precipitate chromium), divides the group as follows:

In strongly Alkaline Solution.		**In Precipitate.**	
Zinc as	$\mathbf{K_2ZnO_2}$	Iron, chiefly as	$\mathbf{Fe_2(OH)_6}$
Alumin. as	$\mathbf{K_2Al_2O_4}$	Manganese as	$\mathbf{Mn(OH)_2}$
		Chromium as	$\mathbf{Cr_2(OH)_6}$
		Cobalt as	$\mathbf{CO(OH)_2}$
		Nickel as	$\mathbf{Ni(OH)_2}$

The solution is tested, in one portion, for *zinc,* by adding ammonium sulphide, which does not precipitate aluminium; in another portion for *aluminium,* by adding ammonium chloride in excess (77), which does not precipitate zinc.

The precipitate is tested, in separate portions, by fusion with oxidizing agents, for *manganese* (identified by the color of the manganate), and for *chromium* (identified by dissolving the mass and from the solution getting colored chromate precipitates). The remainder of the precipitate is tested for *iron,* by dissolving with an oxidizing acid and testing with sulphocyanate.

67. *The plan of separations by the Table at* 127. The group itself is precipitated in two sections, as follows: The use of **ammonium hydrate in excess, with ammonium chloride** precipitates only **Fe, Cr, Al.** But the iron is first obtained in the ferric condition, by use of nitric acid. The zinc (with **Co** and **Ni**) is redissolved by the excess of ammonium hydrate, and the manganese is held in solution by the ammonium salt.

The precipitate of **Fe, Cr,** and **Al** is treated with boiling solution of fixed alkali hydrate in excess, leaving *aluminium* in solution, to be precipitated with ammonium chloride. Of the **Fe** and **Cr** precipitate, a portion is treated with an oxidizing agent to test for *chromium*, and the remainder is dissolved and tested for *iron* with sulphocyanate.

The filtrate from the ammonium hydrate and chloride precipitate is treated with **sulphide**, for precipitation of the remaining **Zn, Mn, (Co, Ni)**. The precipitate is dissolved by hydrochloric acid, so as in the solution to separate *zinc* from *manganese* by excess of fixed alkali hydrate. The manganese is confirmed by oxidation to colored manganate; the zinc, by precipitation, in its alkaline solution, with sulphide. Cobalt and nickel, not easily dissolved from their sulphides with hydrochloric acid, are identified before the blow-pipe.

68. When phosphates are present with fourth-group bases, the phosphates of these bases are precipitated in the third group. For analysis in these cases, see, under Phosphoric Acid, paragraph 301.

Zinc.

69. The following forms of zinc are *in common use:*

Metallic *Zinc*, **Zn**. The coating of "galvanized iron."

Oxide, ZnO.* "Oxide of Zinc," U. S. P. "Commercial Oxide of Zinc," U. S. P. The "zinc white," used as a paint.

Sulphate, $ZnSO_4$. Crystallized, $ZnSO_4.7H_2O$, "Sulphate of Zinc," U. S. P., "White Vitriol."

Chloride, $ZnCl_2$. "Chloride of Zinc," U. S. P., in white crust prepared by melting. Very deliquescent.

Acetate, $Zn(C_2H_3O_2)_2$. "Acetate of Zinc," U. S. P., $Zn(C_2H_3O_2)_2.7H_2O$.

Carbonate, a basic salt.† "Carbonate of Zinc," U. S. P.

70. Zinc *dissolves* in sulphuric acid (diluted with six to ten parts of water) (*a*); in hydrochloric acid (diluted) (*b*), and in solution of alkali hydrate (*c*); in each case with evolution of hydrogen. Nitric acid, moderately dilute, dissolves it with evolution of nitric oxide as the chief by-product (*d*).

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* In *Mineralogy*, Zincite, "Red Zinc Ore," is ZnO. Franklinite is an ore of ferric and manganic oxides, with zinc oxide. Zinc blende or Sphalerite is native sulphide, ZnS.

† In *Mineralogy*, Smithsonite or Calamine is $ZnCO_3$.

$$\begin{array}{llll} a. & Zn + H_2SO_4 & = ZnSO_4 & + 2H\,^{*} \\ b. & Zn + 2HCl & = ZnCl_2 & + 2H \\ c. & Zn + 2KOH & = K_2ZnO_2 & + 2H \\ d. & 3Zn + 8HNO_3 & = 3Zn(NO_3)_2 & + 2NO + 4H_2O \end{array}$$

71. The hydrate (soluble in all alkalies), the sulphide, carbonate (basic), phosphate, arseniate, oxalate, and ferrocyanide are insoluble compounds of zinc, obtained by *precipitation.* The sulphate is the soluble salt most used as a zinc solution in analysis.

72. In solutions of zinc salts, the **alkali hydrates** form a precipitate of *zinc hydrate,* $Zn(OH)_2$, white, redissolved by an excess of the alkali with formation of soluble potassium zincate (or potassium zinc oxide) K_2ZnO_2 (or $K_2O.ZnO$).† Long boiling of the alkali solution tends to reprecipitate the zinc. The precipitate is slightly soluble in ammonium chloride solution.

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* It should be borne in mind by the student, that every true chemical equation is a statement which is good quantitatively as well as qualitatively, and may be translated into parts by weight (grams, ounces, or pounds) by simply adding up the atomic weights (page 13). Taking equation *a*:

$$\begin{array}{ccccccc} Zn & + & H_2SO_4 & = & ZnSO_4 & + & 2H \\ 65 & & 98 & & 161 & & 2 \end{array}$$

That is, 65 ounces of zinc will need just 98 ounces of absolute sulphuric acid to dissolve it, when 161 ounces of zinc sulphate will be made and 2 ounces of hydrogen set free. As to the use of the word part, see paragraph 8. In this operation, the water, used to dilute the sulphuric acid, is not stated in the equation, as it undergoes no chemical change; and the product, 161 parts of zinc sulphate, is dissolved in the same indefinite quantity of water. (Concerning water as a vehicle, see 20.) The student will do well to translate equations into ordinary parts by weight, as a frequent practice.

† If the alkali hydrate be added carefully, drop by drop, without stirring the test-tube, there will be a layer of precipitate with clear alkaline solution above and clear zinc salt solution below. On mixing, with a sufficient addition of alkali, the precipitate nearly or quite all dissolves.

73. Soluble **sulphides**, as $(NH_4)_2S$, precipitate from solutions of zinc salts, also from the alkaline solutions of zinc, *zinc sulphide*, **ZnS**, white, or, when formed in alkaline solutions, gray. Hydrosulphuric acid, in solutions of zinc salts, forms no precipitate, or, in case of zinc acetate and in presence of acetates, only a partial precipitate.*

Soluble **carbonates** precipitate *zinc basic carbonate*, as $Zn_5(OH)_6(CO_3)_2$, white, soluble in ammonium hydrate. **Phosphates** precipitate *zinc phosphate*, $ZnHPO_4$. **Ferrocyanides** precipitate *zinc ferrocyanide*, Zn_2FeCy_6, white; and **ferricyanides** precipitate the *zinc ferricyanide*, $Zn_3(FeCy_6)_2$, yellowish.

74. Before the blow-pipe, on charcoal, when mixed with sodium carbonate, zinc compounds are reduced to the metallic state, but do not appear in metallic form, being vaporized, when the vapor is oxidized by the air and settles as a *coating* of zinc oxide, yellow when hot and white when cold. If this coating, or oxide of zinc from any source, be moistened with solution of **cobalt nitrate** and again ignited, it will be found of green color.

Aluminium.

75. The aluminium compounds † *most common in commerce as chemicals* are:

The Alums: $Al\,K(SO_4)_2.12H_2O$, crystallized "potash alum," "sulphate of aluminium and potassium," U. S. P.; and $Al\,NH_4(SO_4)_2.12H_2O$, "ammonia alum" crystallized, sim-

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* Zinc sulphide is soluble in dilute acids, to an extent preventing its full formation even with the less active acetic acid:

$$Zn(C_2H_3O_2)_2 + H_2S = ZnS + 2HC_2H_3O_2$$

The same fact prevents the precipitation of third-group bases, generally, by the hydrosulphuric acid and free hydrochloric acid used to throw down the second group.

† In *Mineralogy*, Corundum, Sapphire, and Ruby consist of Al_2O_3; Emery, of the same with iron and manganese oxides. Diaspore is aluminium hydrate. Alunite, or alum stone, consists of aluminium and potassium sulphates with aluminium hydrate. Orthoclase, a felspar, is aluminium and potassium silicate. Cryolite is $(NaF)_6Al_2F_6$.

ply "Alum" in the U. S. P. "Concentrated alum" of commerce is the aluminium sulphate which is also pharmacopœial.

The chloride and *bromide,* nominally represented under the trade names "chloralum" and "bromalum," are instable compounds.

The varieties of *Clay* are hydrated aluminium silicates, and Felspars and Felspathic rocks contain double silicates of aluminium with other bases.

Metallic aluminium has been manufactured for use to a limited extent.

76. The hydrate (precipitated by carbonates and by sulphides), and the phosphate, are the principal aluminium *precipitates.* The sulphate is the *solution* most in use.

77. In solutions of aluminium salts, the **alkali hydrates** cause a precipitate of *aluminium hydrate,* $Al_2(OH)_6$, gelatinous, soluble in excess of the fixed alkali hydrates, not dissolved at all by ammonium hydrate. The precipitate dissolves in excess of **KOH** or **NaOH,** by forming *potassium* or *sodium aluminate,* which, in the solid state, is found to be $K_2Al_2O_4$, etc. To dissolve the precipitate takes excess of alkali, beyond **2K** for every Al_2, but just this excess can be neutralized by acid without precipitation. Solution of **ammonium chloride** precipitates the aluminium again as *hydrate* (see 126, note *d*). Soluble **carbonates** make the same precipitate of *aluminium hydrate;*[*] and **sulphides,** also, throw down the *hydrate,*[†]

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[*] $Al_2(SO_4)_3 + 3K_2CO_3 + 3H_2O = Al_2(OH)_6 + 3K_2SO_4 + 3CO_2$

As alum liberates CO_2 from carbonates, it is sometimes used instead of "cream of tartar," in baking powders. This use of alum is not wholesome, as the aluminium hydrate, and especially any excess of alum, is harmful in food. Query: how many parts of crystallized alum will just decompose 100 parts of crystallized sodium carbonate? Taking "ammonia alum" and "bicarbonate of sodium" (83), we have:

$$\underset{453.3}{2NH_4Al(SO_4)_2 12H_2O} + \underset{504}{6NaHCO_3} = Al_2(OH)_6 + (NH_4)_2SO_4 + 3Na_2SO_4 + [6CO_2 + 24H_2O$$

$$504 : 453.3 :: 100 : x = \text{parts bicarb. sodium.}$$

[†] $Al_2(SO_4)_3 + 3(NH_4)_2S + 6H_2O = Al_2(OH)_6 + 3(NH_4)_2SO_4 + 3H_2S$

hydrosulphuric acid making no precipitate. **Phosphates** precipitate *aluminium phosphate,* $Al_2(PO_4)_2$, soluble in fixed alkali hydrates, not easily in acetic acid.*

78. Compounds of aluminium, by ignition on charcoal, with sodium carbonate, leave aluminium oxide, the metal not being liberated. If the oxide be moistened with solution of cobalt nitrate, and again strongly ignited, a blue color is at length obtained.

Iron.

79. The forms of iron in use are very numerous:

Metallic iron. Wrought iron, as in fine iron wire, is the purest form in common use. Steel contains a little carbon in combination as carbide, with other elements. Cast iron contains more carbon, both combined and free, with various impurities.

80. *Ferrous Sulphate,* cryst. $FeSO_4.7H_2O$. "Sulphate of Iron," U. S. P. "Green Vitriol." "Copperas."

81. *Ferrous Sulphide,* **FeS**, material for generating H_2S in the laboratory.

82. *Ferrous Iodide,* FeI_2, in "Syrup of Iodide of Iron" and "Pills of Iodide of Iron," U. S. P.

83. *Ferric Chloride,* Fe_2Cl_6. In "Tincture of Chloride of Iron," U. S. P. ("muriated tincture of iron"). "*Dialyzed Iron,*" a very basic ferric chloride, obtained soluble by dialysis.

84. *Ferric Sulphate,* $Fe_2(SO_4)_3$, in "Solution of Tersulphate of Iron," U. S. P.

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* **Sodium thiosulphate** with boiling precipitates *aluminium hydrate,* with sulphur, sulphur dioxide being given off (a separation from iron). If phosphoric acid and free acetic acid are present, the precipitate is *aluminium phosphate* (also a separation from iron).

85. *Basic Ferric Sulphate,* $\mathbf{Fe_4O(SO_4)_5}$, in "Solution of Subsulphate of Iron," U. S. P., "Monsel's solution."

86. *Ferric Hydrate,* $\mathbf{Fe_2(OH)_6}$, the recent precipitate, "Hydrated Oxide of Iron," U.S.P.; antidote to arsenious acid.

87. *Ferric Oxide* with a little ferrous carbonate, the "Subcarbonate of Iron" of the U. S. P., "sesquioxide of iron." Fe_2O_3

88. *Ores of Iron.* Red Hematite, "specular iron ore," ferric oxide. Magnetic iron ore, ferroso-ferric oxide, $\mathbf{FeO.Fe_2O_3}$, or $\mathbf{Fe_3O_4}$. Sparry or Spathic iron ore, ferrous carbonate.*

89. Iron has two important classes of compounds; the ferrous and ferric. Ferrous compounds exposed to the air oxidize with greater or less rapidity to ferric compounds. (See 99.) Iron is *dissolved*—as a ferrous salt—by dilute sulphuric or hydrochloric acid; as a ferric salt, by moderately dilute (hot) nitric acid.

90. FERROUS COMPOUNDS. The sulphate is the *solution* most in use. The most important *precipitates* are the sulphide, carbonate, phosphate, and ferricyanide, the last named being most distinctive.

91. In solutions of ferrous salts, the **alkali hydrates**, all, cause a precipitate of ferrous hydrate, $\mathbf{Fe(OH)_2}$, which would be white if pure, but in the air appears greenish to black from presence of ferroso-ferric hydrate, and finally changes to red-brown, ferric hydrate. Soluble **Carbonates** precipitate *ferrous carbonate,* $\mathbf{FeCO_3}$ (the preparation of the "carbonate of iron" of the shops), soon changing in the air to reddish-brown ferric hydrate. **Sulphides** (not hydrosulphuric acid) precipitate

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* In *Mineralogy*, Hematite is ferric oxide; Limonite, or brown hematite, is a ferric hydrate; Magnetite is ferroso-ferric oxide; Siderite is ferrous carbonate; Pyrite, iron pyrites, is iron disulphide, $\mathbf{FeS_2}$.

ferrous sulphide, **FeS**, black (the same substance used, when made by melting, to generate **H_2S**). Soluble **Phosphates**, as **Na_2HPO_4**, precipitate *ferrous phosphate*, **$FeHPO_4$**, with **$Fe_3(PO_4)_2$**.

92. Ferricyanides, as **K_3FeCy_6**, with ferrous salts, precipitate *ferrous ferricyanide*, **$Fe_3(FeCy_6)_2$**, deep blue, an important distinction from ferric salts, which give no precipitate though forming a darkened solution. **Sulphocyanates** give no color with ferrous salts strictly free from ferric. **Ferrocyanides**, as **K_4FeCy_6**, precipitate *potassium ferrous ferrocyanide*, **$K_2FeFeCy_6$**, pale blue (the ferric precipitate being deep blue). Both the precipitates named above are insoluble in dilute acids, but decomposed by alkalies (and not obtained if the reaction is alkaline).

93. FERRIC COMPOUNDS. The chloride is the *solution* most in use in analysis. Ferric hydrate, ferrous sulphide, and ferric phosphate, ferrocyanide, and tannate, are among the *precipitates* to be studied. The sulphocyanate red solution is distinctive.

94. In solutions of ferric salts, **alkali hydrates** cause precipitation of *ferric hydrate*, **$Fe_2(OH)_6$**, red-brown (used as an antidote for arsenic). Soluble **carbonates** give the same precipitate of *hydrate.** Soluble **sulphides** precipitate *ferrous sulphide*, **FeS**, with free **S**.† **Phosphates** precipitate *ferric phosphate*, full metallic, **$Fe_2(PO_4)_2$**, scarcely at all soluble in acetic acid (a means of separating **PO_4** from **Ca** and other alkaline earth metals, whose phosphates are easily soluble in acetic acid).

95. Sulphocyanates, as **KCyS**, with ferric salts, give a deep red solution, *ferric sulphocyanate*, **$Fe_2(CyS)_6$**, not a precipitate, but a distinction from ferrous salts. **Ferricyanides** give no blue precipitate (distinction from ferrous salts), the solution becoming green (or, in some conditions, brown).* **Ferrocyanides** cause a precipitate of *ferric ferrocyanide*, $Fe_4(FeCy_6)_3$, ordinary prussian blue. The iron precipitates with the radical $FeCy_6$ are not affected by dilute acids, but are decomposed by alkaline hydrates (and are not formed with mixtures of alkaline reaction).

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* $Fe_2Cl_6 + 3Na_2CO_3 + 3H_2O = Fe_2(OH)_6 + 6NaCl + 3CO_2$

† $Fe_2Cl_6 + 3(NH_4)_2S = 2FeS + S + 6NH_4Cl$

96. Soluble **acetates**, as $NaC_2H_3O_2$, with ferric salts, form *ferric acetate*, giving a dull red color to the liquid without precipitation. On boiling, a precipitate of basic ferric acetate is obtained. **Sulphites**, also, form a red solution, of *ferric sulphite*, decomposed by boiling. **Tannic acid**, and tincture of galls, precipitate ferric salts, blue-black, as ferric tannate, the color substance of ordinary ink. **Salicylic acid** gives a deep violet color; and **meconic** acid, or opium solution, a red color (ferric meconate).

97. IRON SALTS are generally decomposed by **ignition**, but ferric chloride vaporizes undecomposed at a very little above 100° C. (212° F.) Ignition in the air, on charcoal, changes both ferrous and ferric compounds to the *magnetic oxide* (ferroso-ferric), which is attracted to the magnet. For tests with the bead, see 320.

98. DISTINCTIONS BETWEEN FERRIC AND FERROUS COMPOUNDS, most used in analysis:

	Ferric Compounds.	Ferrous Compounds.
(1) Ferricyanides.	No pre. (green color) 95.	*Deep blue pre.*
(2) Sulphocyanates.	*Red sol.*	No change.

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* The test should be so far diluted, in the test-tube, that the analyst can see through it distinctly, when any blue precipitate can be recognized. If the liquid is so concentrated as to be opaque, a blue precipitate cannot be distinguished from the dull green solution.

Other Distinctions, Important in Synthetic Operations:

	Ferric Compounds.	**Ferrous Compounds.**
(3) Carbonates.	Effervescence.	Precip. of carbonate.
(4) Cyanides.	Pre. of hydrate.	Ferrocyanide formed (251).

(5) Oxidizing Agents: **Ferrous Changed to Ferric Co's.**

Nitric acid (238), ...	gives brown gas.
Chlorine water (99 *b*)	is deodorized.
Bromine, ...	"
Permanganate (100), ...	is decolored.

(6) Reducing Agents: **Ferric Changed to Ferrous Co's.**

Hydrosulph. acid, .	deodorized and pre. sulphur.
Sulphides, . . .	see 94.
Sulphurous acid, .	deodorized.

99. *Exercises with Iron in Oxidation and Reduction.*

a. Oxidation with Nitric Acid. Taking a solution of **ferrous salt,** verify it as such, by obtaining the blue precipitate with ferricyanide. Now boil a couple of cubic centimeters (a half fluid dram) of this solution, with five to eight drops of nitric acid, in an evaporating dish, till brown vapor ceases to rise, even after adding another drop of the nitric acid. Take a few drops of the concentrated solution in a test-tube, dilute with water, add ferricyanide, and dilute till transparent. No blue precipitate should appear (95). (For equation of oxidation, see 238.) (Should there be a blue precipitate, add a few more drops of nitric acid, to the remainder in the evaporating dish, and continue the oxidation.)

b. Oxidation with Bromine or Chlorine water. Apply these reagents to ferrous salts in the test-tube, boiling being unnecessary, and test with ferricyanide, before and after the oxidation, as in *a*.

$$2FeCl_2 + 2Cl = Fe_2Cl_6$$

$$6FeSO_4 + 6Cl = 2Fe_2(SO_4)_3 + Fe_2Cl_6$$

$$6FeSO_4 + 3H_2SO_4 + 6Cl = 3Fe_2(SO_4)_3 + 6HCl$$

c. Reduction with Hydrosulphuric Acid: Take a solution of **ferric salt,** verify the absence of ferrous salt by adding ferricyanide to a few drops and diluting, then boil one or two cubic centimeters of the solution, in an evaporating dish, with twice its volume of good solution of hydrosulphuric acid (or pass the gas hydrosulphuric acid for some time through the solution, in a beaker glass). Now test again a few drops of the reduced solution, with ferricyanide, for ferrous salt. Test the solution, before and after reduction, with sulphocyanate, comparing the depth of tints obtained.

$$Fe_2Cl_6 + H_2S = 2FeCl_2 + 2HCl + S$$

d. Reduction with Sulphurous Acid: To a solution of ferric salt, add either sulphurous acid solution (strong enough to bleach litmus-paper) or add a sulphite, as Na_2SO_3, with some hydrochloric acid. Compare the solutions, before and after this treatment, by tests with ferricyanide, and with sulphocyanate, as directed in *c.*

$$Fe_2(SO_4)_3 + H_2SO_3 + H_2O = 2FeSO_4 + 2H_2SO_4$$
$$Fe_2Cl_6 + H_2SO_3 + H_2O = FeSO_4 + FeCl_2 + 4HCl$$

Manganese.

100. The compounds of manganese most used are:

Manganese dioxide, MnO_2; "Binoxide of manganese," U.S.P., found native as Pyrolusite,* and much used as an oxidizing agent, to liberate chlorine, bromine, and iodine, in manufactures, and sanitary measures.†

Potassium Permanganate, $KMnO_4$ (or $K_2Mn_2O_8$), is a salt dissolving with a brilliant purple-red color, an article much used as an oxidizing agent, in analysis, in medicine (permanganate of potassium, U. S. P.) and for disinfecting purposes, as in "Condy's Liquid." It liberates oxygen as ozone. It is deoxidized, and its solutions decolored, by hydrosulphuric acid, sulphurous acid, oxalic acid (268), and other reducing agents.*

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* In *Mineralogy*, Pyrolusite contains MnO_2. It is an ore of manganese, valued by its proportion of dioxide, as an oxidizing agent. Hausmannite is Mn_3O_4; and Braunite, Mn_2O_3. Wad, or "bog manganese," is a hydrate, with other bases.

† $MnO_2 + 4HCl = MnCl_2 + 2Cl + 2H_2O$
$MnO_2 + 2NaCl + 2H_2SO_4 = MnSO_4 + Na_2SO_4 + 2Cl + 2H_2O$
$MnO_2 + 2KI + 2H_2SO_4 = MnSO_4 + K_2SO_4 + 2I + 2H_2O$

Experiments with manganese dioxide as an oxidizing agent. Boil some hydrochloric acid with the MnO_2 in a test-tube. Or, mix NaCl with $MnO_2 + H_2SO_4$ and boil. Chlorine gas is evolved, bleaching litmus-paper. To a dilute solution of potassium iodide add a few drops of dilute sulphuric acid and warm. (The HI formed, by action of the air, very slightly liberates iodine, coloring the solution.) Now add manganese dioxide and warm. Iodine, is much more rapidly liberated, as seen by the color.

101. Manganese may act towards other elements with 2, 3, 4, 6, or 7 bonds (61), but, as a base, it forms stable salts only as a dyad. Manganous sulphate, and chloride, are the more common of the *soluble salts.* The more distinctive tests are the color-substances formed by oxidation, that most used being the fusion to a green mass (103).

102. With solutions of manganous salts, the **alkali hydrates**, all, cause a precipitation of *manganous hydrate*, $\mathbf{Mn(OH)_2}$, white, soon oxidizing in the air to manganic hydrate, brown. The fresh precipitate (before oxidation) dissolves in ammonium chloride solution.† **Sulphides** cause a precipitate of *manganous sulphide*, **MnS**, flesh-colored when free from contamination with iron, etc. **Carbonates** precipitate $\mathbf{MnCO_3}$; phosphates, $\mathbf{Mn_3(PO_4)_2}$.

103. By ignition with alkali carbonate (or hydrate) and an **oxidizing agent**, any manganese compound forms a *bright green mass of manganate* of the alkali metal taken, (as $\mathbf{Na_2MnO_4}$) a delicate and convenient test. The manganese compound is taken in residue by evaporation, or precipitate, or fine powder —the precipitate by excess of fixed alkali hydrate, in the third group work, being sufficiently free from other substances.

Ignite on platinum foil with potassium or sodium nitrate and sodium carbonate.

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* Add H_2S to permanganate of potassium solution and note the decoloring of the solution and the deodorizing of the vapor :

$$8KMnO_4 \text{ (excess)} + 3H_2S = 8MnO_2 \text{ (pre.)} + 3K_2SO_4 + 2KOH + 2H_2O$$

$$2KMnO_4 + 6HCl + 5H_2S \text{ (excess)} = 2KCl + 2MnCl_2 + 8H_2O + 5S \text{ (pre.)}$$

† In the separation by the Table at 127, the ammonium chloride, added with the ammonium hydrate, prevents precipitation of manganese in the first section of the group.

$$3Mn(OH)_2 + Na_2CO_3 + 4NaNO_3 = 3Na_2MnO_4 + 4NO + CO_2 + 3H_2O$$

104. Manganous solution, boiled with **lead dioxide,** or Pb_3O_4, and **nitric acid,** turns red, by formation of permanganate.

105. For bead tests, see 320.

Chromium.

106. The most common chromium compounds are the following:

Chromic oxide, Cr_2O_3, "sesquioxide of chromium,"—the Chrome Green of paints.*

Lead chromate, $PbCrO_4$, the Chrome Yellow of paints.

Potassium dichromate, $K_2Cr_2O_7$ or $K_2CrO_4CrO_3$. "Bichromate of Potassium," U. S. P. "Red chromate of potash."

Potassium chromate, K_2CrO_4, "Yellow chromate of potash."

Chromic anhydride, CrO_3. "Chromic acid," U. S. P.

Chrome alum, $KCr(SO_4)_2 12H_2O$.

107. As a base, chromium acts as Cr_2^{VI}. In chromic acid, H_2CrO_4, the active quantivalence is that of Cr^{VI}. Strong oxidizing agents change the base to some form of chromic acid; reducing agents easily reverse this change.

108. AS A BASE, the chief *solutions* of chromium are those of chromic sulphate, chromic chloride, and potassium chromic sulphate (chrome alum). The most distinctive test is by oxidation to chromate, from which colored precipitates are obtained.

109. With solutions of chromic salts, **alkali hydrates** precipitate *chromic hydrate,* $Cr_2(OH)_6$, green (when dried to Cr_2O_3, "chrome green"), soluble in excess of fixed alkali hydrate if not boiled, the alkaline solution being soon reprecipitated on boiling. Both **sulphides** and **carbonates** precipitate *chromic hydrate.*[*] **Phosphates** precipitate $Cr_2(PO_4)_2$; oxalates cause no precipitation.

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* In *Mineralogy*, Chromite, or chromic iron, is ferroso-chromic oxide, $FeO.Cr_2O_3$, the chief ore of chromium.

110. Chromic salts are oxidized to chromate, for identification of chromium, as follows: (*a*) The precipitate of chromic hydrate (in the third group) is *fused on platinum foil,* with **sodium carbonate** and sodium or potassium nitrate.[†] The mass (yellowish) is dissolved with water, this solution acidulated with acetic acid, and tested with lead salts, etc., for colored precipitates, as by paragraph 112.

(*b*) Chromic salt solutions can be oxidized in alkaline solutions by adding a drop or two of **bromine**, when the tests for chromate are obtained, as in *a*.

111. **CHROMIC ACID, H_2CrO_4,** forms normal salts with nearly all metals, and supersalts with the alkali metals; the normal chromates being mostly yellow, and the dichromates, reddish. The chromates *insoluble* in water are *barium,* manganous, bismuth, mercurous, silver, and *lead.*

112. Solutions of chromates, with **lead salts,** form a precipitate of *lead chromate,* **$PbCrO_4$,** "chrome yellow." With **barium salts,** a yellow precipitate, *barium chromate;* with **silver salts,** a dark reddish precipitate, **Ag_2CrO_4**.

113. Chromates are deoxidized by **reducing agents,** forming chromic base. Hydrosulphuric acid, in acidulated solutions (as in precipitation of the second group), reduces chromate to chromic salt, with some precipitation of sulphur, while the *solution turns green* (*a*). **Ammonium sulphide** (as in precipitation of the third group) forms *chromic hydrate,* so that, *in system-*

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[*] See corresponding equations for aluminium, foot-note to paragraph 77.

[†] $Cr_2(OH)_6 + 2NaNO_3 + Na_2CO_3 = 2Na_2CrO_4 + 2NO + CO_2 + 3H_2O$

atic analysis, chromic acid gives chromium as a base, in third group (*b*). Ferrous salts, with free acid, reduce chromate to chromic salt, a reaction employed in the volumetric estimation of iron (*c*).

a. At first:

$$2K_2CrO_4+10HCl+3H_2S=Cr_2Cl_6+3S+4KCl+8H_2O$$

b. The precipitate may contain some sulphur, but the results are chiefly as follows:

$$K_2Cr_2O_7+(NH_4)_2S_2+4H_2O=Cr_2(OH)_6+K_2S_2O_3+2NH_4OH$$

$$c.\ K_2Cr_2O_7+14HCl+6FeCl_2=Cr_2Cl_6+3Fe_2Cl_6+2KCl+7H_2O$$

114. Chromates, and most other chromium compounds, *ignited on charcoal*, leave *a green mass* of chromic oxide, Cr_2O_3 ("chrome green"). For test in the beads, see 320.

Cobalt.

115. Cobalt is used, in form of *cobaltous oxide*, **CoO**, to color glass blue. The blue glass used to cut off the sodium flame is cobalt-colored glass. The one distinctive and delicate test for cobalt is the bead test (320), in which a glass of melted borax is colored blue. "Smalt" is a pigment of powdered, cobalt-colored glass. "Zaffer" is roasted cobalt ore, used in glass-blowing. A dilute solution of *cobaltous chloride* is used as a "sympathetic ink," writing by which is colorless and invisible when moist from contact with air, but appears distinct, in blue color, on warming at the fire. *Cobaltous nitrate* solution is used in some blow-pipe tests, leaving cobaltous oxide when ignited on charcoal. This oxide, with certain other oxides, enters into combination, with distinctive colors.*

116. The nitrate and chloride are the cobaltous salts most used in *solutions.* Cobaltous solutions are precipitated by **alkali hydrates** as blue basic salts, changing, when boiled, to *cobaltous hydrate,* $Co(OH)_2$, rose-red; but ammonium hydrate, and ammonium salts, dissolve the precipitate (by forming double salts, like magnesium, 57 *a*). **Sulphides** precipitate **CoS,** black, slightly and imperfectly dissolved by dilute acids, and the precipitation is in part obtained with hydrosulphuric acid in normal solutions.

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* In *Mineralogy*, Smaltite (gray cobalt ore) contains cobalt, arsenic, and generally nickel, iron, and copper. Erythrite, "cobalt ochre" or "red cobalt," is cobaltous arseniate. Wad (see Manganese) usually contains cobalt.

117. **Cyanides,** as **KCy,** precipitate *cobaltous cyanide,* easily soluble in excess of the precipitant, as solution of potassio-cobaltous cyanide, $(KCy)_2CoCy_2$. If now a drop or two of hydrochloric acid is added, and the mixture digested, hot, for some time, oxidation occurs, and a *cobalticyanide* is formed, as K_3CoCy_6. In this solution, acids cause no precipitate, a distinction from nickel. **Potassium nitrite,** KNO_2, in somewhat concentrated solution of cobaltous salt, with addition of acetic acid, after long warm digestion, gives a precipitate of *potassium cobaltic nitrite* (distinction from nickel).

118. For the very distinctive bead test, see 320. By ignition, with sodium carbonate on charcoal, a magnetic mass is obtained (Co_3O_4).

Nickel.

119. The metal is much used in an alloy called "German Silver"; copper, 100 parts; nickel, 40 parts, and zinc, 16 parts. Other alloys of nickel are used as a foundation for silver-plating. Electro-plating with nickel is much in use, the pure nickel being deposited from a solution of ammonium nickel chloride or sulphate.*

120. The *solution of nickel* most used is the sulphate. The chloride, also, may be employed. The reactions of nickel most resemble those of cobalt. In absence of **Co,** and **Cu,** nickel is identified in the bead test (320), but not so sharply as cobalt. The separation of nickel from cobalt, by 122, is not free from difficulty.

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* In *Mineralogy,* Niccolite, copper-nickel, or arsenical nickel, is **NiAs,** of a copper-color. Gersdorffite, or nickel glance, is NiS_2NiAs_2.

121. In solutions of nickel salts, the **alkali hydrates** give a pale green precipitate, *nickel hydrate,* $\mathbf{Ni(OH)_2}$, soluble in excess of ammonium hydrate and in ammonium salt solutions (soluble double salts being formed, as with **Mg,** 57 *a*). The precipitate is hardly at all oxidized in the air. **Sulphides,** and $\mathbf{H_2S}$, act with nickel as with cobalt (116). The precipitated *carbonate* is basic, and of green color.

122. In treating nickel solutions with a **cyanide,** as directed in 117 for cobalt, $\mathbf{NiCy_2}$ is precipitated and redissolved as $\mathbf{(KCy)_2NiCy_2}$ like cobalt. Now very slightly acidulating and digesting hot, as directed, no oxidation occurs. A slight addition of dilute acid now decomposes the potassium nickelous cyanide, and precipitates $\mathbf{NiCy_2}$ (separation from cobalt), the precipitate being easily soluble in excess of the acid used.

123. Chlorine water, or solution of hypochlorite, in excess, with warming, precipitates from nickel salts, the black nickelic hydrate.

124. For the bead test, see 320. By *ignition* with sodium carbonate, on charcoal, nickel compounds leave a mass attracted by the magnet.

125. *Exercises with the Third Group of Metals.*

a. Work with a solution of a salt of each base, including ferrous and ferric salts, chromic salts and chromates, following the text for each metal and the Table at 65, and writing equations for all chemical changes.

b. Work the following separations, as directed in the Table at 126. (For Analytical Equations, see 126, *Note f.*):

Al from **Fe_2^{VI}**, in solution of sulphates or chlorides.
Zn " **Mn** " sulphates.
Al " **Cr** " sulphates.

c. Work the following separations, according to the Table at 127 :

Fe'' from **Zn**, in solution of sulphates.
Al " **Co**, " sulphates or other salts.

d. Separate the following metals, as directed in the Tables at 126, and 59 :

Fe_2^{VI} from **Ca**, in a solution of chlorides.
Zn " **Mg**, " sulphates.

(To be sure that the precipitate of Group III., by ammonium sulphide (126), is *complete*, add a drop of the same reagent to the filtrate, when no precipitate should occur. Each group must be *wholly* precipitated and filtered out, to be able to use the filtrate for the following groups.)

e. Separate the following, by the Tables at 127, 59, and 60 (verifying the absence of the fourth group by 59) :

Fe_2^{VI} and **NH_4**, in solution of chlorides.
Al and **K** " sulphates.

126. ANALYSIS OF GROUP III. For Zn, Al, Fe, Mn, Cr, [Co, Ni]. (Separations explained at 66.)

To the Filtrate from Group II., concentrated by evaporation; or, if there are no second-group bases, to the Original Solution; add **Ammonium Chloride,** *then* **Ammonium Hydrate** (*till an alkaline reaction is obtained*), *then* **Ammonium Sulphide** (*enough to complete any precipitate appearing*). (*Note a.*)

Dissolve the well-washed precipitate, on the filter, by cold dilute **Hydrochloric Acid** (Par. 59, note *a*).

Solution: $ZnCl_2$, Al_2Cl_6, $FeCl_2$, $MnCl_2$, Cr_2Cl_6, [$CoCl_2$, $NiCl_2$]. **Residue:** **CoS, NiS,** *black.* (Note *b.*) *Add* **Potassium** *or* **Sodium Hydrate,** *to strong supersaturation* (*using litmus-paper*) *and boil a short time.* (Note *c.*)

Alkaline Solution: Zn and Al. *Test separate portions,*		**Precipitate: $Fe(OH)_2$ and $Fe_2(OH)_6$, $Mn(OH)_2$, $Cr_2(OH)_6$, [$Co(OH)_2$, $Ni(OH)_2$].**			
1. For Zinc.	**2. For Aluminium.**	**3. For Iron [and for Nickel].**	**4. For Manganese.**	**5. For Chromium.**	**6. For Cobalt.** (Note *b.*)
Add **Ammonium Sulphide:** *a precipitate,* **ZnS,** *indicates* **Zinc.**	*Add* **Ammonium Chloride** in excess: *a precipitate,* $Al_2(OH)_6$, *indicates* **aluminium.** (*Note d.*)	*Dissolve a portion of the precipitate with a few drops of* **nitro-hydrochloric acid,** *and expel all free chlorine. Test a portion for iron by* **potassium sulphocyanate:** *a red solut. indicates* **iron** (*Note e*). *Test the Original Solution, for ferrous or ferric form—by* 98.	*Fuse with* Na_2CO_3 and $NaNO_3$, *as directed in* 108; *a green mass,* **manganese.**	*Fuse a portion of the pre. as directed in* 110. *Dissolve in water, acidulate, and test by* 112. *Test Original Solution for Chromic acid, by* 112, *see* 113.	*Test a portion of precipitate in the bead.*
See the text at 73, *and the Table at* 65.	*Follow the text at* 77 *and the Summary at* 65.	*Follow* 65, *and the text at* 89. *For* **Nickel,** *test a portion of sol. by* 122, *etc.*	*Follow the Table at* 65, *and the text at* 102.	*Table at* 65.	

Notes to the Table (126).

Note a. **The filtrate** of this group precipitate, found free from third-group bases by giving no precipitate with a drop of ammonium sulphide, is taken to the Table at 59, for Group IV.

Note b. The residue of undissolved sulphides may be directly tested for **Co** and **Ni**, in the bead; also, may be dissolved with nitro-hydrochloric acid, and tested for nickel (122, etc.) and cobalt (117).

Note c. The supersaturation *must be strong enough* to leave **Zn** and **Al** dissolved (72); boiled long enough to precipitate **Cr** (109), and not boiled very long lest **Zn** be precipitated. In the presence of iron, or manganese, aluminium and zinc are liable to be retained in the precipitate. The precaution may be taken to decant the liquid above the precipitate, dissolve in the least quantity of hydrochloric acid, and again precipitate with *much excess* of alkali hydrate, afterward adding in the decanted liquid.

Note d. $K_2Al_2O_4 + 2NH_4Cl + 4H_2O = Al_2(OH)_6 + 2KCl + 2NH_4OH$
The same result is attained by acidulating with hydrochloric acid, and then making alkaline with ammonium hydrate.

Note e. In the solution by nitro-hydrochloric acid, iron, if present, must be ferric. In the group precipitate, by sulphide, iron must be ferrous (94). The condition of iron is always found by testing the original solution. If the original substance is a solid, a little should be dissolved with hydrochloric acid, and this solution at once tested.

Note f. Examples of Analytical Equations:

(1) $Fe_2Cl_6 + 3(NH_4)_2S = 2FeS + S + 6NH_4Cl$

(2) $FeS + 2HCl = FeCl_2 + H_2S$

(3) $FeCl_2 + 2KOH = Fe(OH)_2 + 2KCl$

(4) $2Fe(OH)_2 + 2Cl + 4HCl = Fe_2Cl_6 + 4H_2O$

(5) $Fe_2Cl_6 + 6KCyS = Fe_2(CyS)_6 + 6KCl$

(1) $ZnSO_4 + (NH_4)_2S = ZnS + (NH_4)_2SO_4$

(2) $ZnS + 2HCl = ZnCl_2 + H_2S$

(3) $ZnCl_2 + 4KOH = K_2ZnO_2 + 2KCl + 2H_2O$

(4) $K_2ZnO_2 + (NH_4)_2S + 2H_2O = ZnS + 2KOH + 2NH_4OH$

127. ANALYSIS OF GROUP III. Alternative Process. (Explanation at 67.)

First Division, **Fe, Cr, Al**; Second Division, **Zn, Mn, Co, Ni.**

To the Filtrate from Group II., freed from **H_2S** *by boiling, or to the Original Solution having no bases of Groups I. and II., add a few drops of* **Nitric Acid** and boil an instant (to oxidize Ferrous salts). *Immediately add* **Ammonium Chloride** *and then excess of* **Ammonium Hydrate.*** *If a precipitate occurs, filter and wash, reserving the filtrate for Group III.,* **B.**

Precipitate, Group III., A : $Fe_2(OH)_6$, $Cr_2(OH)_6$, $Al_2(OH)_6$.

Pierce the point of the filter, and with a little water rinse the precipitate into a test-tube; *add* **Potassium** *or* **Sodium Hydrate,** *and boil several minutes.* If a residue remains, filter, and wash.

Precipitate : $Fe_2(OH)_6$, $Cr_2(OH)_6$.		**Solution : $K_2Al_2O_4$.**
For Iron, dissolve the precipitate in a little **hydrochloric acid,** and test the solution with **sulphocyanate.** Test the Original Solution for ferrous and ferric forms of iron, by 98.	**For Chromium,** fuse a portion of the precipitate as directed in 110; dissolve in water, acidulate, and test for chromate by 112. Test the original solution for chromate, by 112. (See 113.)	**For Aluminium,** add to the alkaline solution, **ammonium chloride.** Or, acidulate, and then add excess of ammonium carbonate. A precipitate is $Al_2(OH)_6$.

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* There must be sufficient excess to redissolve the zinc (72), cobalt, and nickel.

Filtrate, Group III., B : Contains Zn, Mn, Ni, Co.

Add **Ammonium Sulphide,** *and if a precipitate appears, warm until it subsides. Filter and wash, reserving the filtrate for Group IV.*

Precipitate : ZnS, MnS, NiS, CoS.

Treat, on the filter, with cold dilute hydrochloric acid. If a black residue remains, leave it on the filter. Boil the filtrate.

Residue : NiS, COS.*		**Solution : $ZnCl_2$; $MnCl_2$.**	
		Add a decided excess of **Potassium** or **Sodium Hydrate,** and digest without warming. Filter.	
For Cobalt, test the residue by the blow-pipe, in the bead (320).	**For Nickel,** test the residue by the blow-pipe, in the bead (320). In presence of Cobalt, dissolve the residue with nitro-hydrochloric acid, and test by the text, 122.	**Precipitate : $Mn(OH)_2$.***	**Solution : K_2ZnO_2.**
		For Manganese, fuse the precipitate as directed in 103.	**For Zinc,** add **ammonium sulphide :** precipitate, **ZnS.**

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* Small portions of nickel and cobalt may be dissolved from the sulphides, by **HCl**, and then will precipitate with the **$Mn(OH)_2$**. That precipitate may be tested, in the bead, for **Ni** and **Co**, as above directed.

128. Group II. Metals whose Sulphides are insoluble in dilute acids.

Group I. is included within this group.

For Analytical Study in this Work.		**Of less frequent occurrence.**	
Copper, . .	$\mathbf{Cu}''$	Gold,	$\mathbf{Au}'''$
Bismuth, . .	$\mathbf{Bi}'''$	Platinum,	$\mathbf{Pt}^{IV}$
Lead, . . .	$\mathbf{Pb}''$	Palladium,	$\mathbf{Pd}''$
Silver, . .	$\mathbf{Ag}'$	Ruthenium,	$\mathbf{Ru}_2{}^{VI}$, $\mathbf{Ru}^{VI}$
Mercury,	$\mathbf{Hg}''$, in mercuric co's.	Iridium,	$\mathbf{Ir}_2{}^{VI}$, $\mathbf{Ir}^{IV}$
	$\mathbf{Hg}_2{}''$, in mercurous co's.	Rhodium,	$\mathbf{Rh}_2{}^{VI}$
Arsenic,	$\mathbf{H_3As'''O_3}$, arsenious acid.	Osmium,	$\mathbf{Os}_2{}^{VI}$
	$\mathbf{H_3As^{V}O_4}$, arsenic acid.	Tellurium,	$\mathbf{Te}''$, $\mathbf{Te}^{IV}$, $\mathbf{Te}^{VI}$
Antimony,	$\mathbf{Sb}'''$, in antimonious co's.	Selenium,	$\mathbf{Se}''$, $\mathbf{Se}^{IV}$, $\mathbf{Se}^{VI}$
	$\mathbf{Sb}^{V}$, in antimonic co's.	Tungsten,	$\mathbf{W}^{VI}$
Tin,	$\mathbf{Sn}''$, in stannous co's.	Molybdenum,	$\mathbf{Mo}^{IV}$, $\mathbf{Mo}^{VI}$
	$\mathbf{Sn}^{IV}$, in stannic co's.	Cadmium,	$\mathbf{Cd}''$

129. The metals of this group have less chemical power, as bases, than those of the other groups; they oxidize or tarnish less readily in the air, and they are more easily reduced from their oxides or salts to the metallic state. The "noble metals" or precious metals are in this group. Silver, gold, mercury, platinum, and palladium are obtained in the metallic state simply by heating their oxides short of redness. In most cases, the only acid which will dissolve the metals of this group is nitric acid; and gold and platinum require nitro-hydrochloric acid for solution. Arsenic and selenium are metalloids rather than metals. Mercury, arsenic, and antimony easily vaporize.

130. Comparison of Bismuth, Copper, and Cadmium.

Taken in solution of their chlorides, nitrates, sulphates, or other soluble salts.

	Bismuth.	**Copper.**	**Cadmium.**
KOH or **NaOH, in excess.**	*White pre.*	*Blue black pre.*	*White pre.*
NH_4OH, in excess.	*White pre.*	*Deep blue solution.*	*Colorless solution.*
Dilution with water.	*White pre. (basic salt).*	*No change.*	*No change.*
Sulphides, and H_2S	*Black pre.* *(Insol. in Cyanide).*	*Black pre.* *(Sol. in Cyanide).*	*Yellow pre.* *(Ins. in Cyanide).*
Iron or **Zinc.**	*Spongy pre.*	*Copper coating.*	*Gray sponge.*
Grape-sugar, KOH, and heat.	*Black pre.*	*Yellow-brown pre.*	. . . . . .

Copper.

131. *Common forms :* *

Metallic Copper ; Brass, an alloy of copper and zinc ; Bronze, an alloy of copper and tin.

Copper Sulphate, **$CuSO_4$**. Crystallized, **$CuSO_4 5H_2O$**, "Sulphate of Copper," U. S. P., "Blue Vitriol."

Copper basic Acetate, **$Cu_3O(C_2H_3O_2)_4.6H_2O$**, "Subacetate of copper," U. S. P., "Verdigris."

132. The sulphate is the *solution* most used. The solutions are bluish, unless very dilute. The most important *precipitates* are—*metallic copper,* the hydrate, sulphide, and ferrocyanide. The ammonic *blue solution* is distinctive. *Copper is dissolved* by nitric acid (238*b*). *Cuprous salts,* as **Cu_2Cl_2** (combinations of **Cu_2''**), are very instable. Cuprous hydrate and oxide are obtained in some tests.

133. Solutions of copper salts, with **fixed alkali hydrates,** precipitate *copper hydrate,* **$Cu(OH)_2$**, dark blue to black, insoluble in excess of precipitants. **Ammonium hydrate** precipitates the same, very easily soluble in excess of the alkali, the solution having a very deep blue color, a test for copper. **Carbonates** precipitate basic salts ; **sulphides,** and **H_2S**, precipitate *copper sulphide,* **CuS**, black ; **ferrocyanides** give a brown precipitate, **Cu_2FeCy_6** ; **cyanides,** as **KCy**, give a pale greenish precipitate, **$CuCy_2$**, easily soluble by excess of the reagent to **$(KCy)_2CuCy_2$**.

Arsenites, as **K_3AsO_3**, with copper sulphate, give a green precipitate, *copper arsenite,* chiefly **$CuHAsO_3$**, "Scheele's Green": with copper acetate, a green precipitate of *copper aceto-arsenite,* **$3Cu(AsO_2)_2.Cu(C_2H_3O_2)_2$**, "Schweinfurth Green," the most common form of "Paris Green." The precipitates are obtained from a solution of arsenious acid carefully neutralized with an alkali, but they are soluble in ammonium hydrate and decomposed by fixed alkalies.

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* *Mineralogy :* Copper is found native, and as Chalcocite or Copper Glance, **CuS**; Chalcopyrite or Copper Pyrite, **CuS**, **FeS**, **FeS_2**; Bornite or Purple Copper, copper and iron sulphide ; Cuprite or Red Oxide of Copper, **CuO** ; Malachite, **$Cu_2(OH)_2CO_3$**; and Chrysocolla, a silicate.

134. A strip of bright (not rusted) **iron,** or **zinc,** immersed a short time in a solution of copper salt, receives a bright copper coating (a distinctive and delicate test).

$$CuSO_4 + Fe = Cu + FeSO_4.$$

For every 63.3 parts of copper deposited, 56 parts of iron (or 65 parts of zinc) are dissolved off, as shown by the equation with reference to the atomic weights.

135. *Ignition* of copper compounds, with sodium carbonate, on charcoal, leaves metallic copper in finely divided grains :

$$2CuSO_4 + 2Na_2CO_3 + C = 2Cu + 2Na_2SO_4 + 3CO_2$$

For the bead test, see 320.

Bismuth.

136. In the *metallic state,* bismuth is used in "fusible metal" (bismuth, lead, and tin), and other alloys. The metal is found native.

Bismuth basic nitrate, $BiONO_3$. "Subnitrate of Bismuth," U. S. P.

Bismuth basic carbonate. $Bi_2O_2CO_3$. "Subcarbonate of Bismuth," U. S. P.

Bismuth basic chloride, or *oxychloride,* $BiOCl$. "Pearl White."

137. The compounds of trivalent bismuth (Bi''') are more specifically termed *bismuthous* compounds, to distinguish them from quinquivalent bismuth compounds (of Bi^v), designated as bismuthic. The latter are mostly very instable. *The metal is dissolved* by nitric acid.

138. Most of the "soluble salts" of bismuth only partially dissolve in pure water, requiring acidulated water for full solution. The *solutions* most used are the normal nitrate ("the poisonous nitrate") in water acidulated with nitric acid, and the normal chloride dissolved in water acidulated with hydrochloric acid. **Water**, added to bismuth, out of proportion to the free acid present, decomposes the normal salt, and gives white precipitates of *basic chloride*, $BiOCl$, *basic nitrate*, $BiONO_3$, or other basic salt:

$$BiCl_3 + H_2O = BiOCl + 2HCl$$
$$Bi(NO_3)_3 + H_2O = BiONO_3 + 2HNO_3$$

139. Bismuth solutions, with **alkali hydrates**, precipitate *bismuth hydrate*, $Bi(OH)_3$, white, insoluble in excess of the reagents (with ammonium hydrate, a separation from copper). **Carbonates** precipitate *basic carbonate*, $Bi_2O_2CO_3$, the "subcarbonate" of medicine. **Hydrosulphuric acid**, and sulphides, precipitate Bi_2S_3, black. **Chromates** (normal and super salts) precipitate *basic chromate*, $Bi_2O(CrO_4)_2$, yellow, distinguished from lead chromate by not dissolving with fixed alkali. **Phosphates** precipitate $BiPO_4$, white, less easily soluble by nitric acid than other phosphates, so that free phosphoric acid precipitates bismuth nitrate acidulated solution (not bismuth chloride acidulated solution). In solutions of bismuth salts containing only just enough acid to prevent precipitation, **iodides** cause some precipitate of $BiOI$ with formation of HI.

140. *Ignition* on charcoal, with sodium carbonate, leaves metallic bismuth in little lustrous globules, brittle under the knife or hammer (the brittleness, a distinction from lead). A yellow incrustation of oxide forms on the charcoal, about the globules.

$$2Bi_2O_3 + 3C = 6Bi + 3CO_2$$
$$4BiONO_3 + 2Na_2CO_3 + 3C = 4Bi + 4NaNO_3 + 5CO_2$$

141. Comparison of First Group Metals : Pb, Ag, Hg_2'' [Hg''].

In solution of their Nitrates or Acetates.

	Lead.	Silver.	Mercurous Base.	Mercuric Base.
KOH or NaOH in excess.	*Solution* (144).	*Gray pre.*, Ag_2O.	*Black pre.*, Hg_2O.	*Yellow pre.*, HgO.
NH_4OH in excess.	*White pre.* (144).	*Solution.*	*Black pre., a salt of* $(NH_2Hg_2)'$.	*White pre., a salt of* $(NH_2Hg)'$.
Chlorides and HCl.	*Pre. sparingly soluble in water.*	*Pre. dissolved by* NH_4OH.	*Pre., blackened by* NH_4OH.	*No pre.*
Bromides.	*Pre.*	*Pre.*	*Pre.*	*Pre.* from mercuric nitrate, not chloride.
Iodides.	*Yellow pre.*	*Pre., dissolved in excess of iodide.*	*Pre.* (153).	*Yellow to red pre., sol. in excess iodide.*
H_2SO_4 and sulphates.	*White pre.*	*No pre.*	. . . .	. . . .
Chromates.	*Yellow pre.*	*Red pre.*	*Yellow pre.*	. . . .
Metallic Zinc.	*Gray pre.*	*Gray black pre.*	*Gray pre.*	*Gray pre.* (157).
Stannous chloride.	$PbCl_2$	$AgCl$, *then* Ag.	Hg.	Hg_2Cl_2, *then* Hg.

Lead. (First Group Metals: **Pb, Ag,** $\mathbf{Hg_2''}$).

142. Common Forms: *

Metallic Lead and its alloys. Tinner's solders contain lead.

Lead basic Carbonate. "White Lead."

Lead oxide, **PbO.** "Litharge." "Massicot." Plumbic oxide.

Triplumbic tetroxide, Pb_3O_4. "Red Lead."

Lead dioxide, PbO_2. Brown. Native, brilliant crystals, Plattnerite.

Lead Chromate, $PbCrO_4$. "Chrome Yellow."

Lead Acetate, $Pb(C_2H_3O_2)_2$. Crystallized, $Pb(C_2H_3O_2)_2 3H_2O$, "Sugar of Lead"; "Acetate of Lead," U. S. P.

Lead basic Acetate, chiefly $Pb_3O_2(C_2H_3O_2)_2$. "Solution of Subacetate of Lead," U. S. P.; "Goulard's Solution."

143. In the permanent salts of lead, the metal acts as a dyad. The acetate and nitrate are the only *soluble salts* in use. The sulphide, chloride, sulphate, and chromate, are the *precipitates* most important in analysis. *In the First Group, very few of the salts are soluble in water.*

The metal is dissolved by nitric acid used pretty dilute: the strong acid does not dissolve it.

144. *Solutions of lead salts give precipitates* as follows:

With **Fixed alkali hydrates,** *lead hydrate,* $Pb(OH)_2$, soluble in excess of the alkali.

Ammonium hydrate, *lead hydrate,* $Pb(OH)_2$ scarcely formed with lead acetate.

Carbonates, *lead basic carbonate,* as $(PbCO_3)_2Pb(OH)_2$, white.

$\mathbf{H_2S}$ **and Sulphides, PbS,** black, insoluble in dilute acids or in alkalies.

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* *Mineralogy:* Galenite or Galena, **PbS**; Cerussite, $PbCO_3$; Pyromorphite, $3Pb_3(PO_4)_2.PbCl_2$; Plattnerite, lead dioxide.

H_2SO_4 and Sulphates, $PbSO_4$, white, slightly soluble in strong acids.*

HCl and Chlorides, $PbCl_2$, white, somewhat soluble in cold water, more soluble in hot water, separated by hot water from **AgCl** and **Hg_2Cl_2**. **Lead cannot be removed in the first group.**

Bromides, $PbBr_2$, white, somewhat soluble.

Iodides, PbI_2, yellow, somewhat soluble in excess of precipitant.

Chromates, $PbCrO_4$, yellow, dissolved by fixed alkalies (distinction from bismuth chromate).

Phosphates, $Pb_3(PO_4)_2$, white, insoluble in dilute acetic acid.

Oxalates, PbC_2O_4, white.

Sulphites, $PbSO_3$, white.

145. On charcoal, with sodium carbonate, by ignition, lead globules are obtained, malleable under the hammer and soft under the knife (distinction from bismuth), while a yellow incrustation of lead oxide forms around the mass. The reduction of sulphate, on charcoal, is as follows:

$$2PbSO_4 + 2Na_2CO_3 + C = 2Pb + 2Na_2SO_4 + 3CO_2$$

Meanwhile, some of the alkali sulphate is reduced:

$$Na_2SO_4 + 2C = Na_2S + 2CO_2$$

In a crucible, without charcoal, there is simple transposition without reduction, but with dissociation of **$PbCO_3$**:

$$PbSO_4 + Na_2CO_3 = Na_2SO_4 + PbO + CO_2$$

See, further, under Sulphuric Acid, 285. This fusion with sodium carbonate is used, in analysis, to obtain solutions. The fused mass is treated with water and this solution tested for the acid (SO_4), when the residue is dissolved by an acid (HNO_3 for lead) and this solution tested for the base (321, *fifth* clause).

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* On diluting the solution of lead sulphate in strong acids, the lead sulphate is precipitated again. The sulphuric acid of commerce frequently becomes turbid when diluted with water, owing to lead sulphate being present as an impurity.

Silver.*

146. *Metallic Silver* is used mostly in alloy with a small proportion of copper—the U. S. coin standard being 90 per cent. silver and 10 per cent. copper. In plated wares, the coating is pure silver. The salt in use is,

Silver Nitrate, $\mathbf{AgNO_3}$, crystallized (anhydrous) in the "Nitrate of Silver" of the U. S. P., obtained vitreous by melting, as in "Fused Nitrate of Silver," U. S. P., or "Lunar Caustic." In solution, used as an indelible ink (149).

147. *The metal dissolves* with nitric acid. The only *solution* of silver used in ordinary analysis is the nitrate. The chloride *precipitate* and its solubility in ammonium hydrate are of first importance in the analysis of silver salts, or of chlorides. Unlike lead, silver can be wholly removed in Group I. The sulphide and iodide are frequent precipitates in analysis; and the reduction of silver by metallic copper, etc., should be well studied.

148. *Solutions of silver salts give precipitates* as follows, on adding—

Fixed alkali hydrate, *silver oxide,* $\mathbf{Ag_2O}$, gray, not soluble in excess.

Ammonium hydrate, *silver oxide,* $\mathbf{Ag_2O}$, soluble in excess.

$\mathbf{H_2S}$ **and Sulphides,** *silver sulphide,* black.

HCl and Chlorides, *silver chloride,* white, easily soluble in ammonium hydrate as ammonio silver chloride, $\mathbf{(AgCl)_2(NH_3)_3}$, scarcely at all soluble in nitric acid, the **First Group Precipitate.** (Equations in 204 *a.*)

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* *Mineralogy:* Silver is found native. Argentite is silver sulphide; Pyrargyrite is represented by $(Ag_2S)_3Sb_2S_3$; and Cerargyrite, or Horn Silver, is silver chloride.

Bromides, *silver bromide,* **$AgBr$**, white with yellowish tint.

Iodides, *silver iodide,* pale yellow, soluble in excess of **KI** or **NaI**, forming **$KIAgI$**, etc.

Cyanides, **$AgCy$**, white, soluble in excess, as **$KCyAgCy$**, etc. "Cyanide of Silver," U. S. P.

Carbonates, **Ag_2CO_3**, white, soluble by **NH_4OH**.

Phosphates, **Ag_3PO_4**, light yellow, soluble by **NH_4OH**.

Chromates, **Ag_2CrO_4**, dull red.

Oxalates, **$Ag_2C_2O_4$**, white. Detonates when heated, dry.

149. Silver is easily deoxidized. A bright strip of **copper,** in solution of **$AgNO_3$**, becomes coated with lustrous metallic silver, while copper nitrate enters into solution. (Compare with 134, and write an equation for this reduction corresponding with that.) Silver chloride, acidulated, is reduced by **zinc.** **Ferrous salts** reduce silver as **Ag** in brown-black precipitate, while ferric salt is formed. A *silver mirror* lining may be made in a test-tube or a flask, by treating therein a solution of silver nitrate with either of the following: (1) A little of solution of chloral hydrate and then very small additions of ammonium hydrate; (2) solution of potassium tartrate to precipitate, then ammonium hydrate to dissolve nearly all the precipitate, then warming on the water bath; (3) ammonium hydrate to nearly dissolve the precipitate at first formed, then a little dilute alcoholic solution of oils of cloves and cinnamon. *Organic fabrics and tissues, under the influence of light,* reduce silver from its salts to black argentous oxide, **Ag_4O**, and to metallic silver, black—these making the stain of silver salts, on the skin or hair or on cloth. The stain is gradually removed by the solvent action of potassium cyanide (poisonous) or of sodium hyposulphite (thiosulphate). Silver nitrate, for medicinal solutions, should be dissolved in distilled water, melted ice being next best. Water containing organic matter, as rain-water, will hold silver nitrate in solution very much longer if protected from the light.

150. Ignition on charcoal with sodium carbonate gives globules of metallic silver.

Mercury.

151. *Common forms:*

Mercury, the liquid metal. Quicksilver. Finely divided and slightly oxidized, in "Pills of Mercury," U. S. P., or "Blue Mass," and "Mercury with Chalk," U. S. P.

Mercurous Chloride, Hg_2Cl_2 (or $HgCl$). "Mild Chloride of Mercury," U. S. P.; "Calomel"; "Subchloride of Mercury"; "Protochloride of Mercury."

Mercuric Chloride, $HgCl_2$. "Corrosive Chloride of Mercury," U. S. P.; "Corrosive Sublimate"; "Bichloride of Mercury"; "Protochloride of Mercury."

Mercurous Iodide, Hg_2I_2. "Green Iodide of Mercury," U. S. P.

Mercuric Iodide, HgI_2. "Red Iodide of Mercury," U. S. P.

Mercurous Oxide, Hg_2O, black. In "black wash."

Mercuric Oxide, HgO, red. In "yellow wash."

Mercuric Sulphide, HgS. "Vermilion."*

Mercuric Nitrate, $Hg(NO_3)_2$. In "Solution of Nitrate of Mercury," U. S. P.

152. The only **MERCUROUS** salt much used in *solution* is the *nitrate*, $Hg_2(NO_3)_2$, somewhat instable, requiring free acid to prevent decomposition by water, and almost sure to contain mercuric salt. The chief *precipitate* and insoluble mercurous compound is the *chloride*, Hg_2Cl_2 (blackened by alkalies).

Mercury is dissolved by nitric acid, mercurous salt forming by excess of mercury; mercuric salt, when nitric acid is in excess.

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* In *Mineralogy*: Cinnabar, HgS.

153. *Solutions of Mercurous Salts,* with

Fixed alkali hydrates, precipitate *mercurous oxide,* $\mathbf{Hg_2O}$, black.

Ammonium hydrate,—*mercurosammonium salt,* as $\mathbf{NH_2Hg_2\text{-}NO_3}$, or from chloride, $\mathbf{NH_2Hg_2Cl}$.* (" Amido-mercurous chloride.") Black.

Sulphides and $\mathbf{H_2S}$,—$\mathbf{Hg_2S}$ and **HgS,** black, insoluble in nitric acid.

HCl and Chlorides,—*mercurous chloride,* $\mathbf{Hg_2Cl_2}$, " calomel," **First Group Precipitate,** changed by ammonium hydrate into $\mathbf{NH_2Hg_2Cl}$, black.

Bromides,—$\mathbf{Hg_2Br_2}$, yellowish white.

Iodides,—$\mathbf{Hg_2I_2}$ (green), with $\mathbf{HgI_2}$ (yellow to red), soluble by excess of **KI**, except a brown residue of **Hg**.

154. **Stannous Chloride** precipitates, from mercurous nitrate, first $\mathbf{Hg_2Cl_2}$, white, then, by more stannous salt, a dark precipitate of **Hg** is formed, with stannic salts, $\mathbf{Sn(NO_3)_4}$ and $\mathbf{SnCl_4}$, in solution. See 157, as to this and other reductions.

155. The **MERCURIC** Salt chiefly used in *solution* is the chloride. The nitrate requires acidulated water for complete solution. The oxide, mercurammonium chloride, sulphide, iodide, and metallic mercury, are characteristic *precipitates.* Mercury is readily identified in the dry way, by 158.

156. *Precipitations of Mercuric Salts :*

Fixed alkali hydrate, HgO, reddish to yellow, "yellow oxide of mercury," U. S. P.; " red precipitate."

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* The substitution of $\mathbf{Hg_2}''$ for $\mathbf{2H'}$ in the base ammonium ($\mathbf{NH'H'H'H'}$, or $\mathbf{NH'H'Hg'\text{-}Hg'}$).

Ammonium hydrate, *mercurammonium salt,* **NH_2HgCl** * with the chloride, *white,* the "ammoniated mercury" of the U. S. P., "white precipitate," "amido-mercuric chloride."

H_2S and Sulphides, HgS, black, passing through shades of orange and brown before completely formed. With insufficient **H_2S**, the precipitate dissolves on shaking. This substance, when dried and triturated with heat, turns red (manufacture of "vermilion"). It dissolves by nitrohydrochloric acid (not by nitric acid).

Iodides, *mercuric iodide,* **HgI_2**, yellow to red, soluble by excess of **KI**, forming **$(KI)_2HgI_2$**, (and other soluble potassio-mercuric iodides) used as a reagent in precipitating ammonium hydrate (in absence of free acid), also a general precipitant of alkaloids (even in presence of free acid).

157. **Stannous Chloride,** gradually added to Mercuric Chloride, precipitates first *mercurous chloride,* **Hg_2Cl_2**, white, then **Hg**, dark gray:

$$2HgCl_2 + SnCl_2 = Hg_2Cl_2 + SnCl_4$$
$$HgCl_2 + SnCl_2 = Hg + SnCl_4$$

The metallic precipitate, warmed with hydrochloric acid and triturated under the glass rod, unites in globules of mercury.

A clean strip of **copper,** in solution of any mercury compound, becomes coated with mercury, silver-white when gently rubbed.

158. *Before the blow-pipe,* all forms of mercury readily vaporize. Any compound of mercury, mixed with **sodium carbonate** (the mixture dry), when heated in a test-tube held obliquely over the flame, yields a sublimed coating of metallic

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* Substitution of **Hg''** for **$2H$** in the base **NH_4** (**$NHHHg''Cl$** instead of **$NHHHHCl$**).

mercury in the outer part of the tube. This coating, when cool, rubbed with a glass rod, yields little globules of mercury. Mercury oxides give this result by heat alone; but the chlorides require an alkaline base to unite with the chlorine, otherwise the chlorides sublime undecomposed:

$$HgCl_2 + Na_2CO_3 = Hg + O + 2NaCl + CO_2$$

159. Comparison of Arsenic, Antimony, and Tin.

Taken as Solutions of Arsenious acid, Antimonious chloride, and Stannous chloride.

	As'''	Sb'''	Sn''
H_2S forms colored Sulphides, soluble in yellow ammonium sulphide, and in alkalies, then reprecipitated by acids :	As_2S_3, yellow, insoluble by HCl, soluble by $(NH_4)_2CO_3$. Dissolved by chlorine, as $H_3AsO_4(As^V)$.	Sb_2S_3, orange, soluble by strong HCl, insoluble by $(NH_4)_2CO_3$.	SnS, brown (SnS_2, yellow), soluble by HCl, insoluble by $(NH_4)_2CO_3$.
NH_4OH, in excess :	No precipitate.	Pre., Sb_2O_3, white.	Pre., $Sn(OH)_2$, white.
Zn and dilute H_2SO_4:	AsH_3 (gas). In silver solution, pre. Ag, leaving H_3AsO_3 in solution.	SbH_3 (gas). In silver solution, precipitates Ag_3Sb.	Sn, a gray mass, in the generator, along with the zinc.
	Flame of the gas leaves spots on porcelain, soluble in hypochlorite.	Flame of the gas leaves spots on porcelain, insoluble in hypochlorite.	
Dilution with water:	. . . .	Precipitate of $SbOCl$.	Precip. of Sn_2OCl_2.
Concentrated Nitric Acid, acting on the solids:	Forms H_3AsO_4, giving most of the precipitates of H_3PO_4.	Forms Sb_2O_4 and Sb_2O_5, insoluble.	Forms SnO_2, insoluble.

Arsenic.

160. *Common Forms:*

Arsenious oxide, $\mathbf{As_2O_3}$. "Arsenious Acid," U. S. P. "White Arsenic." "Ratsbane." In solution with potassium acid carbonate, as potassium arsenite, in "Solution of Arsenite of Potassium," U. S. P., or "Fowler's Solution."

Arsenious Sulphide, $\mathbf{As_2S_3}$. "Orpiment."[*] "King's Yellow."

Copper Aceto-Arsenite, $3Cu(AsO_2)_2.Cu(C_2H_3O_2)_2$. "Paris Green." "Schweinfurth Green."

161. Arsenic is most common in its trivalent form, as $\mathbf{As'''_2O_3}$, etc., but its most stable compounds are those of quinquivalent arsenic, as $\mathbf{Na_3As^{V}O_4}$. The *solution* in common use is that of $\mathbf{As_2O_3}$, or, when dissolved, $\mathbf{H_3AsO_3}$; a solution requiring much water. With hydrochloric acid, the arsenious oxide dissolves more abundantly; with alkalies, it is freely soluble.

Arsenic is identified by the results of "Marsh's Test"; by ignition with charcoal; by the green cupric precipitate, etc. Arsenic is not a base, though it needs be separated from the bases in analysis, and as the arsenites and arseniates of alkali metals are soluble in water, *alkaline hydrates and carbonates, etc., do not precipitate arsenic.*

162. Solutions of **Arsenious** oxide (or of $\mathbf{H_3AsO_3}$) and of arsenites, with **hydrosulphuric acid**, the solution being acidified with hydrochloric acid, form a yellow precipitate of *arsenious sulphide*, $\mathbf{As_2S_3}$ (*a*). The precipitate scarcely at all dissolves in hydrochloric acid, dissolves by chlorine (action of nitro-hydrochloric acid, or of chlorate of potassium with hydrochloric acid), forming $\mathbf{H_3AsO_4}$ (*b*), and dissolves (in division of the second group) by ammonium sulphide (*c*); also, slowly, by ammonium carbonate.

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[*] *Mineralogy*: Orpiment, $\mathbf{As_2S_3}$; Realgar, $\mathbf{As_2S_2}$; Arsenopyrite, or Mispickel, $\mathbf{FeS_2FeAs_2}$.

a. $2H_3AsO_3 + 3H_2S = As_2S_3 + 6H_2O$

or $As_2O_3 + 3H_2S = As_2S_3 + 3H_2O$

b. $As_2S_3 + 10Cl + 8H_2O = 2H_3AsO_4 + 3S + 10HCl$

c. $As_2S_3 + 3(NH_4)_2S = 2(NH_4)_3AsS_3$ * (variable).

163. Solution of **copper sulphate** with arsenious acid, on a *slight* addition of NH_4OH to neutralize the acid, gives a green precipitate of *copper arsenite*, $CuHAsO_3$ (see 133). Excess of ammonia dissolves the precipitate. Solution of **silver nitrate**, in like manner neutralized, precipitates *silver arsenite*, Ag_3AsO_3, yellow.

164. Marsh's test is an example of the reducing action of zinc, or other metal taken. When hydrogen is generated, by action of zinc and a metal (70 *a*), in presence of As_2O_3, the **H** first unites with the **O**, forming water; then **H** unites with **As**, forming the gas AsH_3. In similar manner, hydrogen with any compound of arsenic will generate arsenious hydride:

$$Zn + H_2SO_4 = ZnSO_4 + 2H$$

$$As_2O_3 + 12H = 3H_2O + 2AsH_3$$

$$As_2O_3 + 6Zn + 6H_2SO_4 = 6ZnSO_4 + 3H_2O + 2AsH_3$$

$$H_3AsO_3 + 3Zn + 3H_2SO_4 = 3ZnSO_4 + 3H_2O + AsH_3$$

To conduct the operation, place in the generator of Marsh's apparatus three or four cubic centimeters (about a fluid dram) of a mixture of one part of sulphuric acid and eight to ten parts of water. Add some granulated zinc, add the solution to be tested for arsenic (free from chlorine), at once close the appara-

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* Ammonium sulpharsenite, a sulphur salt corresponding to the tribasic oxysalt, $(NH_4)_3AsO_3$. The ammonium sulphide solution is precipitated with acids, as the original As_2S_3, with free sulphur:

$$2(NH_4)_3AsS_3 + 6HCl = As_2S_3 + 6NH_4Cl + 3H_2S.$$

tus and immediately * conduct the escaping gas into a little solution of silver nitrate, by immersing the delivery-tube therein. If arsenic (or antimony) is present, there will be a black precipitate—**Ag** in case of arsenic ($\mathbf{SbAg_3}$ in case of antimony). When enough precipitate is obtained—but not until the air is expelled from the apparatus †—the delivery-tube may be taken out of the solution, and the gas at once lighted at the orifice. Hold cold porcelain in the flame, when arsenic separates in lustrous dark steel-gray spots, and antimony in velvety black spots:

$$2AsH_3 + 3O = 2As + 3H_2O$$

The spots of arsenic are soluble in solution of sodium hypochlorite ‡ ("chlorinated soda"), the antimony spots not soluble in this reagent. The material subjected to Marsh's test must be free from oxidizing agents, sulphides, and from organic matter. To ensure that the chemicals and apparatus are free from arsenic, conduct a blank operation with them.

165. The action of arsenious hydride in silver nitrate solution is represented by this equation, **Ag** being precipitated and arsenious acid left in solution.

$$AsH_3 + 6AgNO_3 + 3H_2O = 6Ag + H_3AsO_3 + 6HNO_3$$

(Compare $\mathbf{SbH_3}$, 178.) Now, a yellow precipitate by hydrosulphuric acid in this solution gives conclusive evidence of arsenic, but it is first necessary to filter out the black precipitate of **Ag**, and then * necessary to remove all the silver nitrate left undecomposed by the gas, adding just enough hydrochloric acid to complete the white precipitate, **AgCl**, and filtering this out. (Avoid excess of **HCl**, as this dissolves a trace of silver.) If there remains any silver nitrate in solution, the yellow arsenic precipitate will be darkened, or even blackened, by it.†

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* Arsenious hydride gas is a deadly poison. Its escape into the air is prevented by first delivering into the silver solution where it decomposes, and then, when the air is carried out so that the gas will not explode, burning the gas. If the apparatus enables the arsenic solution to be introduced into the generator after the gas has been running a while, it may be lighted even before, and directly after the arsenic solution is introduced.

† Any combustible gas, mixed with air in due proportions, explodes when ignited. Kerosene explosions are caused by vapor of the oil, mixed with air, and ignited. Even very fine and combustible dust, well mixed with air, will explode when lighted, as has occurred in grain mills. If there is no air in the generator, the gas of Marsh's test may be lighted as safely as city gas at any gas-burner.

‡ This solution is not good unless it bleaches litmus-paper.

166. Metallic **aluminium**, and excess of strong solution of potassium or sodium hydrate, with compounds of arsenic, on boiling the mixture to start the reaction, give arsenious hydride gas,—a distinction and separation from antimony. Phosphoric acid gives PH_3, interfering with this test. The sulphide of arsenic will serve in this test.

167. If the narrow delivery-tube of Marsh's apparatus be heated to redness, while arsenious hydride is passing, free arsenic will be deposited on the surface of the tube as a *mirror coat.* The mirror is beyond the flame in case of arsenic; before the flame in case of antimony.

168. Arsenious compounds are oxidized to arsenic compounds, as As_2O_5 or H_3AsO_4, by nitric acid, chlorine, bromine, permanganate, and a large number of oxidizing agents.

169. All compounds of arsenic, *ignited with sodium carbonate*, on charcoal, give the *garlic odor* of vaporized elemental arsenic. If, in a small tube closed at one end, dried arsenical material be introduced to the closed end, a fragment of charcoal pressed down upon it, on igniting first the charcoal and then the material, a mirror of **As** forms above the heated part, and the garlic odor is obtained. Arsenious oxide sublimes unchanged, in absence of charcoal and other reducing agents, forming octahedral crystals (microscopic).

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* Observe that $SbAg_3$ is dissolved by **HCl**.

† The "analytical equations" for arsenic, in the work of separation by 187, may be given as follows :

(1) $2H_3AsO_3 + 3H_2S = As_2S_3 + 6H_2O$
(2) $As_2S_3 + 3(NH_4)_2S = 2(NH_4)_3AsS_3$
(3) $2(NH_4)_3AsS_3 + 6HCl = As_2S_3 + 6NH_4Cl + 3H_2S$
(4) $As_2S_3 + 28Cl + 20H_2O = 2H_3AsO_4 + 3H_2SO_4 + 28HCl$
or $As_2S_3 + 10Cl + 8H_2O = 2H_3AsO_4 + 3S + 10HCl$
(5) $H_3AsO_4 + 4Zn + 4H_2SO_4 = 4ZnSO_4 + AsH_3 + 4H_2O$
(6) $AsH_3 + 6AgNO_3 + 3H_2O = 6Ag + H_3AsO_3 + 6HNO_3$

170. Arsenic Acid, $\mathbf{H_3AsO_4}$, forms salts closely resembling the phosphates, in solubilities and many other properties. At a moderate heat, it is changed to arsenic oxide, or anhydride, $\mathbf{As_2O_5}$, which bears a dull red heat without change; but the alkaline arseniates are unchanged at full red heat (in absence of charcoal and other reducing agents).

Arsenic acid, be it observed, is the form of arsenic obtained in dissolving arsenious sulphide (whether by nitric acid or chlorine).

171. Arsenic acid is but very slowly precipitated by **hydrosulphuric acid,** full precipitation requiring twenty-four hours' treatment with the gas in warm solution. Little or no color is obtained at first (a distinction from arsenious acid). The precipitate is a reduction to arsenious sulphide, $\mathbf{As_2S_3}$, with free sulphur,—arsenic sulphide not being formed. For solubilities of the precipitate, see 162.

In Marsh's test, the reaction is nearly as prompt as with arsenious acid:

$$\mathbf{H_3AsO_4 + 4Zn + 4H_2SO_4 = 4ZnSO_4 + 4H_2O + AsH_3}$$

172. In solutions of arseniates, **magnesium salts,** with ammonium chloride and hydrate, precipitate *ammonium magnesium arseniate*, $\mathbf{MgNH_4AsO_4}$ (a distinction from arsenites). **Silver nitrate** precipitates $\mathbf{Ag_3AsO_4}$, reddish-brown. **Ammonium molybdate,** in solution with acid, gives a yellow precipitate, like that with phosphates (distinction from arsenite).

173. As reducing agents, sulphurous acid and thiosulphates, oxalic acid, and stannous chloride, change arsenic acid to arsenious forms.

Antimony.

174. *Common Forms:*

Metallic antimony in certain alloys,—lead and antimony being type-metal, and tin with antimony, britannia metal.

Antimonious Chloride, $SbCl_3$. "Butter of antimony."

Antimonious Sulphide, Sb_2S_3. Native,* it is black, the "Sulphuret of Antimony" of the U. S. P., or "black antimony," that mostly sold under this name at present being nearly or quite destitute of any compound of antimony. The "*Oxysulphuret*," U. S. P., "kermes mineral," is brown to reddish-brown. "Golden sulphuret" is Sb_2S_5.

Potassio Antimonious Tartrate, $KSbOC_4H_4O_6$; "Tartrate of Antimony and Potassium," U. S. P.; "Tartar Emetic" or "Tartarized Antimony."

175. The most stable compounds of antimony are the antimonious (those of Sb'''). Antimonic compounds contain Sb^v, some of which are stable in the solid state. The *solution* most used is that of antimonious chloride, requiring free acid, as pure water decomposes a part of the salt (176). The tartrate, however, and the potassio tartrate, dissolve in water without acidulation. *The solvent for the metal* is dilute nitro-hydrochloric acid.

Antimony is identified by its precipitation with water, the color and solubilities of its sulphide, and especially by Marsh's test.

176. Antimonious chloride solution, not containing too much free hydrochloric acid (like bismuth and tin), is precipitated by addition of sufficient **water**, as *antimonious oxychloride*, **SbOCl**, soluble in hydrochloric acid.

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* *Mineralogy:* Stibnite is Sb_2S_3; Jamesonite contains antimony, lead, and other metals, combined with sulphur.

177. Solutions of **Antimonious Salts**, with **alkali hydrates**, precipitate *antimonious oxide*, Sb_2O_3 ("Oxide of Antimony," U. S. P.), soluble in excess of fixed alkalies, not readily soluble in excess of ammonium hydrate.

Hydrosulphuric acid, best added to a moderately acidulated solution, precipitates *antimonious sulphide*, Sb_2S_3, orange, soluble in strong hydrochloric acid, scarcely at all in solution of ammonium carbonate (two ways of separating from arsenious sulphide). The precipitate dissolves in (yellow) **ammonium sulphide** (in common with arsenic and tin, in the division of the second group)—the solution containing ammonium sulphantimoniate, $(NH_4)_3SbS_4$, from which acids precipitate the orange *antimonic sulphide*, Sb_2S_5.

178. **In Marsh's test**, conducted exactly as directed for arsenic, in 164, the gas *antimonious hydride*, SbH_3, is obtained, but less readily than with arsenic, the antimony being at first reduced to **Sb**, remaining in the generator, and gradually uniting with nascent hydrogen to form the gas.

$$SbCl_3 + 3Zn + 3HCl = 3ZnCl_2 + SbH_3$$

$$SbCl_3 + 3Zn + 3H_2SO_4 = 3ZnSO_4 + 3HCl + SbH_3$$

In passing the gas into **silver nitrate** solution, if antimonious chloride is used, the action should be moderated by using sufficiently dilute acid, and the generator kept cool, to prevent undue precipitation of the silver as a chloride, white, by the hydrochloric acid carried over. The antimony enters into the precipitate, $SbAg_3$:

$$SbH_3 + 3AgNO_3 = SbAg_3 + 3HNO_3$$

The precipitate should be filtered out, boiled with hydrochloric acid, the mixture well diluted and filtered; the filtrate will give, with hydrosulphuric acid, an orange precipitate, evidence of antimony.

As to the *spots* of **Sb** left by the flame of antimonious hydride upon cold porcelain, see 164.

179. *By ignition* on charcoal, with sodium carbonate, all compounds of antimony are reduced to metallic antimony, forming rough brittle globules if the material is in a considerable quantity, but the reduced metal vaporizes and oxidizes at the same time, the white oxide rising in abundant vapors and coating the support.

Tin.

180. Tin in the free state is in extensive use as a coating of sheet-iron in "tin plate," and as "block tin." "Pewter" is tin alloyed with a little antimony.

Stannous Chloride, $\mathbf{SnCl_2}$; the crystals, with $\mathbf{2H_2O}$, "tin salt," used as a mordant in dyeing.

Stannic Chloride, $\mathbf{SnCl_4}$. "Butter of Tin." Used in dyeing, to brighten red colors, etc.

Stannic Sulphide, $\mathbf{SnS_2}$. "Mosaic Gold." "Polisher's Putty" or "Putty Powder" is a crude stannic oxide.*

181. The proper *solvents* of metallic tin are, to make stannous salts, hot hydrochloric acid, or very dilute nitric acid; to make stannic salt, nitro-hydrochloric acid. *The solutions in analytical use* are, for stannous salts, acidulated solution of stannous chloride (a reagent much employed in reductions), and, for the tetrad condition, stannic chloride. By exposure to air, stannous chloride changes to stannic compounds, a change retarded by putting a bit of metallic tin in the bottle.

Tin is characterized (with antimony and bismuth) by precipitation with water; separated (with arsenic and antimony) by the solution of its sulphide precipitate in ammonium sulphide, and separated from arsenic and antimony by its deposition in the generator of Marsh's apparatus.

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* *Mineralogy:* Cassiterite, stannite, tin-stone,—chiefly stannous oxide.

182. Stannous chloride solution, not containing too much free acid, is precipitated white, on addition of **water**, Sn_2OCl_2 *stannous oxychloride.* **Alkali hydrates** precipitate *stannous hydrate*, $Sn(OH)_2$, white, soluble in excess of fixed alkali hydrates by forming stannites (as K_2SnO_2), but insoluble in ammonium hydrate. **Carbonates** precipitate *stannous hydrate.*

183. Hydrosulphuric acid (and sulphides) precipitate, from stannous solutions, *stannous sulphide*, **SnS**, brown (stannic sulphide is yellow). The precipitate dissolves in **yellow ammonium sulphide** (not easily in colorless ammonium sulphide, see 22)—soluble sulphostannates being formed, as $(NH_4)_2SnS_3$—a separation with antimony and arsenic from the other members of group second. The alkaline sulphide solution, with acids, is precipitated yellow as stannic sulphide, SnS_2 (see equation in note to 162 *c*).

184. Tin is reduced by **zinc**, in acidulated solutions, as in Marsh's test, the *metallic tin* appearing as a gray spongy mass or dark gray powder. The reduction, in Marsh's test, is more complete if a piece of platinum foil be put in the generator with the zinc. If all the zinc is allowed to dissolve the tin may then dissolve, and the filtered solution may be tested for tin, with mercuric salt, as below. But the work for tin is best done, after Marsh's test for **As** and **Sb**, by dissolving the fine zinc and all the powdery residue in the generator with hot and moderately dilute hydrochloric acid (filtering to get a clear solution) and testing the solution, for stannous salt, with **mercuric chloride** (see 157).

185. Stannous salts are *oxidized* to stannic salts whenever the former are used as reducing agents, as with mercury salts, silver salts, ferric salts, etc.; by exposure to the air, and by nitric acid, chlorine, etc.

By ignition, on charcoal, with sodium carbonate (and, better, with potassium cyanide) tin is easily reduced, from its compounds, to lustrous malleable globules, a slight white incrustation of stannic oxide being formed.

186. ANALYSIS OF GROUP I. For **Pb, Ag, Hg_2''**.

To the Original Solution add **Hydrochloric Acid,** *a drop at a time, as long as precipitation occurs; warm, agitate, and filter.* Reserve the Filtrate, for Group II. (18[illegible]

Precipitate: Group I.: **$PbCl_2$, AgCl, Hg_2Cl_2.**

Wash the precipitate slightly with cold water on the filter; then treat it with much ho[illegible]r.

Solution: $PbCl_2$.	**Precipitate undissolved: AgCl, Hg_2Cl_2.** *Digest with warm, slightly diluted* **Ammonium Hydrate.**	
Test for lead by adding **Sulphuric acid:** White pre., **$PbSO_4$.** **Hydrosulphuric acid:** Black pre., **PbS.** **Chromate** [illegible]llow pre., **$PbCrO_4$.** **Iodides:** [illegible] pr[illegible] *If lead is present, it will be found in second group, and must be removed there, before testing for third group.*	**Solution (filtrate): $(NH_3)_2(AgCl)_2$.** *Test for Silver, after expelling any excess of ammonium hydrate by boiling, by acidulating slightly with* **Nitric Acid.** A precipitate is **AgCl.**	**Residue: NH_2Hg_2Cl,** *black.* (Lead basic salt, *white.*)
See the text at 144, *and the Table at* 141.	*See text at* 147, *and Table at* 141.	*See the text at* 152, *and Table at* 141.

187. ANALYSIS OF GROUP II. For As, Sb, Sn ; Pb, (Ag), Bi, Cu, (Cd) ; Hg.

To the Filtrate from Group I. (or the original solution + **HCl** if Group I. is absent) *add excess of* **Hydrosulphuric Acid**, *warm and filter.* Reserve the Filtrate (which must give no precipitate with **H_2S**) for Group III. (126 or 127.)

Precipitate : As_2S_3 (yellow), **Sb_2S_3** (orange), **SnS** (brown) or **SnS_2** (yellow), **PbS** (black), **Ag_2S** (black), **Bi_2S_3** (black), **CuS** (black), **CdS** (yellow), **HgS** (finally black).

Wash the precipitate thoroughly on the filter, and digest it with yellow **Ammonium Sulphide** (*Note a*).
Wash the residue and reserve it for Group II. B. **The Solution : As, Sb, Sn, Sulphosalts** (*Note b*).
Acidulate [illegible] *Solution with Hydrochloric Acid, add hydrosulphuric acid, filter and wash well.*

Precipitate : Group II., A. As_2S_3, Sb_2S_5, SnS_2, free sulphur.

Digest the washed precipitate, in a test-tube (*Note c*) *in hot* **hydrochloric acid with potassium chlorate** (*a minute fragment*), *till the precipitate is dissolved (or decolored). Filter out any sulphur, rinsing the filter, receive the filtrate in an evaporating-dish and by gentle heat expel from it all free chlorine* (*Note d*).

Transfer to the generator of Marsh's Apparatus (**Solution : H_3AsO_4, $H_4Sb_2O_7$, $SnCl_4$**), *and make Marsh's Test* (164), *receive all the gas in solution of* **Silver Nitrate.** *Filter the silver solution, and wash the precipitate.*

In the Generator : Sn (Sb, Zn).	Precipitate from SbH_3 : $SbAg_3$(Ag).	Solution fr. AsH_3: H_3AsO_3($AgNO_3$).
As directed in 184, *dissolve the solid contents with hydrochloric acid and test the (filtered) solution for* **Stannous** *salt, by* **Mercuric Chloride.**	*Digest with hot* **Hydrochloric Acid** *to dissolve* **antimony** (178) *and test by* **H_2S** : *an orange precipitate.* **Water** : *a white precipitate.*	*As directed in* 165, *remove the silver by adding just enough very dilute hydrochloric acid and filtering.* *Test for* **arsenic** *by* **H_2S** : *a yellow precipitate. Marsh's test spots, free* [illegible] *solution. Ignition* (169).
See the Table at 159.	*See the Text at* 177, *and Table at* 159.	*See the Table at* 159.

GROUP II., B.—PbS, (Ag_2S), Bi_2S_3, CuS, CdS, HgS, free sulphur.

The well-washed precipitate, insoluble in $(NH_4)_2S_2$, *is treated with hot, moderately dilute* **Nitric Acid** *to dissolve, and the solution evaporated to expel excess of acid.* (*Note e.*)

<table>
<tr><td rowspan="3">Residue : HgS (black), free S, ($PbSO_4$).
<i>Dissolve the black precipitate by</i> nitro-hydrochloric acid, <i>and expel free chlorine by boiling.</i>
Solution : $HgCl_2$.
<i>Test for</i> mercury <i>by</i> Stannous Chloride, 157.
Test with Cu, 157, and by 158.</td><td colspan="4">Solution : $Pb(NO_3)_2$, ($AgNO_3$), $Bi(NO_3)_3$, $Cu(NO_3)_2$, $Cd(NO_3)_2$.
<i>To a portion of the solution, add a drop of very dilute</i> Sulphuric Acid, <i>for</i> Lead. <i>If a precipitate appears, add to the whole solution, to remove all the lead, and filter.</i></td></tr>
<tr><td rowspan="2">Precipitate : $PbSO_4$.
<i>Add</i> chromate <i>for yellow precipitate.</i>
<i>Test by</i> 145.</td><td colspan="3">Filtrate (or Solution not precipitated by H_2SO_4) : Bi, Cu, Cd, salts.
<i>Expel excess of acid, if any, by evaporation.</i>
<i>Add</i> Ammonium Hydrate <i>to a slight alkaline reaction</i>, 133.</td></tr>
<tr><td>Precipitate : $Bi(OH)_3$.
<i>Confirm by dissolving in a very little</i> HCl <i>on a watch-glass, and adding water.</i></td><td>Blue Solution : <i>Copper.</i> (<i>Note a.</i>)
<i>Concentrate in an evaporating dish, acidify with acetic acid, and test with</i> ferrocyanide.
<i>Test this, or Original Solution, with</i> metallic iron.</td><td>Colorless Solution : May contain <i>Cadmium.</i>
<i>In absence of copper, to the concentrated solution add</i> H_2S : <i>a yellow precipitate indicates</i> CdS.
<i>If copper is present, treat the sulphides with</i> KCy. <i>Precipitate not dissolved, indicates cadmium.</i></td></tr>
<tr><td><i>See Table at</i> 141, <i>and Text at</i> 152.</td><td><i>Table at</i> 141. <i>Text at</i> 143.</td><td><i>Text at</i> 138. <i>Table at</i> 130.</td><td><i>Text at</i> 132. <i>Table at</i> 130.</td><td><i>Table at</i> 130.</td></tr>
</table>

187. ANALYSIS OF GROUP II. For As, Sb, Sn ; Pb, (Ag), Bi, Cu, (Cd) ; Hg.

To the Filtrate from Group I. (or the original solution + **HCl** if Group I. is absent) *add excess of* **Hydrosulphuric Acid**, *warm and filter*. Reserve the Filtrate (which must give no precipitate with **H_2S**) for Group III. (126 or 127.)

Precipitate : **As_2S_3** (yellow), **Sb_2S_3** (orange), **SnS** (brown) or **SnS_2** (yellow), **PbS** (black), **Ag_2S** (black), **Bi_2S_3** (black), **CuS** (black), **CdS** (yellow), **HgS** (finally black).

Wash the precipitate thoroughly on the filter, and digest it with yellow **Ammonium Sulphide** (*Note a*).

Wash the residue and reserve it for Group II. B. **The Solution : As, Sb, Sn, Sulphosalts** (*Note b*).

Acidula[illegible] *Solution with Hydrochloric Acid, add hydrosulphuric acid, filter and wash well.*

Precipitate : Group II., A : As_2S_3, Sb_2S_5, SnS_2, free sulphur.

Digest the washed precipitate, in a test-tube (*Note c*) *in hot* **hydrochloric acid with potassium chlorate** (*a minute fragment*), *till the precipitate is dissolved* (*or decolored*). *Filter out any sulphur, rinsing the filter, receive the filtrate in an evaporating-dish and by gentle heat expel from it all free chlorine* (*Note d*).

Transfer to the generator of Marsh's Apparatus (**Solution : H_3AsO_4, $H_4Sb_2O_7$, $SnCl_4$**), *and make Marsh's Test* (164), *receive all the gas in solution of* **Silver Nitrate**. *Filter the silver solution, and wash the precipitate.*

In the Generator : Sn (Sb, Zn).	**Precipitate from SbH_3 : $SbAg_3$(Ag).**	**Solution fr. AsH_3: H_3AsO_3($AgNO_3$).**
As directed in 184, *dissolve the solid contents with hydrochloric acid and test the (filtered) solution for* **Stannous** *salt, by* **Mercuric Chloride.**	*Digest with hot* **Hydrochloric Acid** *to dissolve* **antimony** (178) *and test by* **H_2S** : *an orange precipitate.* **Water** : *a white precipitate.*	*As directed in* 165, *remove the silver by adding just enough very dilute hydrochloric acid and filtering.* *Test for* **arsenic** *by* **H_2S** : *a yellow precipitate. Marsh's test spots, from* [illegible] *solution. Ignition* (169).
See the Table at 159.	*See the Text at* 177, *and Table at* 159.	*See the Table at* 159.

GROUP II., B.—PbS, (Ag_2S), Bi_2S_3, CuS, CdS, HgS, free sulphur.

The well-washed precipitate, insoluble in $(NH_4)_2S_2$, *is treated with hot, moderately dilute* **Nitric Acid** *to dissolve, and the solution evaporated to expel excess of acid.* (*Note e.*)

Residue : HgS (black), **free S**, $(PbSO_4)$. *Dissolve the black precipitate by* **nitro-hydrochloric acid**, *and expel free chlorine by boiling.* **Solution : $HgCl_2$.** *Test for* **mercury** *by* **Stannous Chloride**, 157. Test with **Cu**, 157, and by 158.	**Solution : $Pb(NO_3)_2$, $(AgNO_3)$, $Bi(NO_3)_3$, $Cu(NO_3)_2$, $Cd(NO_3)_2$.** *To a portion of the solution, add a drop of very dilute* **Sulphuric Acid**, *for* **Lead.** *If a precipitate appears, add to the whole solution, to remove all the lead, and filter.*			
	Precipitate : $PbSO_4$. *Add* **chromate** *for yellow precipitate.* *Test by* 145.	**Filtrate** (or Solution not precipitated by H_2SO_4) : **Bi, Cu, Cd,** salts. *Expel excess of acid, if any, by evaporation.* *Add* **Ammonium Hydrate** *to a slight alkaline reaction,* 133.		
		Precipitate : $Bi(OH)_3$. *Confirm by dissolving in a very little* **HCl** *on a watch-glass, and adding water.*	**Blue Solution :** *Copper.* (*Note a.*) *Concentrate in an evaporating dish, acidify with acetic acid, and test with* **ferrocyanide.** *Test this, or Original Solution, with* **metallic iron.**	**Colorless Solution :** **May contain** *Cadmium.* *In absence of copper, to the concentrated solution add* H_2S *: a yellow precipitate indicates* **CdS.** *If copper is present, treat the sulphides with* **KCy.** *Precipitate not dissolved, indicates cadmium.*
See Table at 141, *and Text at* 152.	*Table at* 141. *Text at* 143.	*Text at* 138. *Table at* 130.	*Text at* 132. *Table at* 130.	*Table at* 130.

Notes to Table for Analysis of Group II. (187.)

Note a. Pierce the point of the filter, rinse the precipitate into the test-tube with the reagent, digest in the test-tube, afterward filtering if a residue remains. Use as little of the solvent as possible (*Note a. to Table at* 59). *As to the solvent,*—Ammonium Sulphide is open to this objection, it dissolves some *copper sulphide*, whereby a false indication of Group II., **A.**, may be obtained, and traces of copper lost altogether. **Sodium Sulphide** may be used instead of ammonium sulphide, but this dissolves **HgS**. Uncertainty as to copper may be settled by testing the original solution with metallic iron.

Note b. If there is doubt whether the precipitate has at all dissolved in the alkaline sulphide, a little of it is acidulated, when a colored precipitate signifies **As, Sb,** or **Sn,**—a white precipitate, unless undue excess of $(NH_4)_2S_2$ was used, indicates no **As, Sb,** or **Sn,**—only sulphur:

$$2(NH_4)_3AsS_3 + 6HCl = As_2S_3 \text{ (yellow)} + 6NH_4Cl + 3H_2S$$
$$(NH_4)_2S_2 + 2HCl = S \text{ (white)} + 2NH_4Cl + H_2S$$

Note c. The **HCl** alone does not dissolve As_2S_3 (162), but **HCl** with $KClO_3$ (a bit as large as a pin's head) gives free **Cl**, which dissolves all these sulphides, to the forms given in the Table. The sulphur of the sulphides may partly remain undissolved as a light-colored residue. Nitro-hydrochloric acid can be used instead of chlorate with hydrochloric acid.

Note d. Free **Cl** will counteract reduction in Marsh's test. When wet litmus-paper is no longer bleached in the steam, the chlorine is sufficiently removed. In rinsing into the generator, if there is any white residue (as **SbOCl**, etc.) carefully transfer it all to the generator.

Note e. Over action of nitric acid may oxidize **PbS** to insoluble $PbSO_4$, therefore given under the head of mercury, but unless strong nitric acid is used, lead will hardly be lost in this way. See 277.

Note f. Analytical Equations for bismuth, and mercury:

(1) $2Bi(NO_3)_3 + 3H_2S = Bi_2S_3 + 6HNO_3$

(2) $Bi_2S_3 + 8HNO_3 = 2Bi(NO_3)_3 + 3S + 4H_2O + 2NO$

(3) $Bi(NO_3)_3 + 3NH_4OH = Bi(OH)_3 + 3NH_4NO_3$

(1) $HgCl_2 + H_2S = HgS + 2HCl$

(2) $HgS + 8Cl + 4H_2O = HgCl_2 + H_2SO_4 + 6HCl$

(3) $HgCl_2 + SnCl_2 = Hg + SnCl_4$

188. *Exercises with Second Group Metals, and with metals of different groups.*

a. Work with a solution of a salt of each member of the group, following the text, with constant observation of the Tables for Comparison: at 130, for **Bi, Cu, Cd**; at 141, for **Pb, Ag, Hg_2'', Hg''**; at 159, for **As, Sb, Sn.** Write equations for all chemical changes in this work.

b. Find the bases of each of the following salts, working their solutions, as would be done with unknown material, by the Tables at 186 and 187: Lead acetate solution, Mercuric chloride solution, Copper Sulphate solution, Arsenious acid solution, Antimonious chloride solution, Stannous chloride solution. Write equations, as fully as possible, for all the changes occurring in these analytical operations.

c. Work the following separations, as directed in the Tables at 186 and 187:

Solution of **$Pb(C_2H_3O_2)_2$**, with **$AgNO_3$**, and **$Hg_2(NO_3)_2$**.
Solution of **$Pb(C_2H_3O_2)_2$**, with **$Bi(NO_3)_3$**, and **$Cu(NO_3)_2$**.
Solution of **$PbCl_2$**, with **$HgCl_2$**.
Solution of **H_3AsO_3**, with **$SbCl_3$** (and **HCl** to dissolve).
Solution of **H_3AsO_3**, with **$SbCl_3$**, and **$SnCl_2$** (with **HCl**).

d. Separate the following metals:

Cu from **Fe''**, as sulphates (187 and 126).
Pb (as nitrate) from **Ca** (as nitrate), (186, 187, 126, 59).
Base from acid, in **K_3AsO_3** solution (187, 126, 59, 60).
Ag from **Ba**, as nitrates (186, 187, 126, 59).
Cu from **Al**, and **Mg**, as sulphates (187, 126, 59).
Hg'' from **Zn**, and **NH_4**, as chlorides (187, 127, 59).

e. Separate the bases in the following mixtures, by methods other than those of the Tables of this work:

Ag from **Fe_2^{VI}**, in solution of nitrates:
  (1) By a chloride (identifying the iron).
  (2) By an iodide " "
  (3) By ammonium hydrate (identifying the iron and silver).
  (4) By metallic zinc " " "

Cu from **Ba**, in solution of chlorides, by at least four different plans, identifying each metal, and not using the same reagent for *separation* a second time.

Bi from **Zn**, in solution of chlorides, by as many different plans as may be found.

Hg from **Al**, in solution of chlorides, by as many different plans as may be found.

Gold.

189. Coin Gold, U. S. standard, is 90 per cent. gold and 10 per cent. copper. An alloy of gold and silver is silver-color even when having 40 per cent. of gold, and so little as 2 per cent. of silver makes the alloy brass-color. Pure gold is not affected by nitric acid, but quickly dissolves as **$AuCl_3$**, auric chloride, by action of nitro-hydrochloric acid or free chlorine. An alloy of gold-copper or gold-silver having not over 20 per cent. of gold is disintegrated by nitric acid (of 20 per cent.), the gold being separated undissolved.

190. The chief salt of gold is auric chloride, no oxy-salts being formed, and aurous compounds (those of **Au'**) being instable. Gold is most easily separated and distinguished by its reduction to free metal. Solutions to be tested for gold may be tested at once by adding **oxalic acid** and ammonium oxalate and setting aside a short time, when all the gold is reduced (platinum and palladium not reduced), and the filtrate can then be worked for the successive group precipitates.

191. In solution of auric chloride, **$AuCl_3$**, **fixed** alkalies cause no precipitate (owing to formation of soluble double chlorides), but **ammonium hydrate** precipitates ammonia aurate, **$(NH_3)_2Au_2O_3$**, reddish-yellow, "fulminating gold." **Hydrosulphuric acid** precipitates *auric sulphide*, **Au_2S_3**, black, changed by boiling to brown *aurous sulphide*, **Au_2S**, both slowly **soluble in ammonium sulphide.** This solution is precipitated by acids, so that, if not first removed by oxalic acid (190), gold will be separated *with* **As, Sb,** *and* **Sn,** *in Group I.* All **reducing agents** precipitate gold, **Au,** brown to violet, the washed precipitate made compact and lustrous by trituration. **Ferrous sulphate, Oxalic acid,** and **Stannous chloride** are used as reducing agents, the precipitate formed by the latter containing tin oxides and being known as "purple of Cassius."

Platinum.

192. "Platinum black" is platinum precipitated from alkaline solution by alcohol; "platinum sponge" is a porous, slightly coherent condition of the metal obtained by ignition of ammonio-platinic chloride. Platinum is insoluble in nitric acid, and slowly dissolved by nitro-hydrochloric acid or other form of free chlorine, forming platinic chloride, $\mathbf{PtCl_4}$. The metal requires the heat of the oxy-hydrogen blow-pipe for fusion.

193. Preservation of Platinum Vessels.

(1) *Melted metals*, reducible metallic compounds ignited on charcoal, or ignited with reducing agents, quickly alloy with platinum, melting foil or wire at once.

(2) *Free chlorine and bromine* attack platinum at ordinary temperatures. Free *sulphur, arsenic, phosphorus, and iodine* attack ignited platinum. Hence, fusion of sulphides, etc., with reducing agents, is more or less injurious to platinum.

Platinum surfaces are cleaned by fusing borax on them; also, by digestion with nitric acid.

194. In solution of platinic chloride, $\mathbf{PtCl_4}$, alkaline hydrates do not precipitate platinum as a hydrate, but form double salts, as potassio-platinic chloride, $\mathbf{(KCl)_2PtCl_4}$, the potassio and ammonio double salts being only slightly soluble in water. These are precipitated best by adding potassium and ammonium chlorides. **Hydrosulphuric acid**, and sulphides, slowly precipitate *platinic sulphide*, $\mathbf{PtS_2}$, black, **soluble in ammonium sulphide** (along with **As, Sb, Sn**). Reduction is not effected by oxalic acid (distinction from gold), but is accomplished slowly by ferrous sulphate, and rapidly by zinc,—in each of these instances the metal being obtained in black powder.

Before the blow-pipe, compounds of platinum are reduced to spongy platinum.

Palladium.

195. The forms of this metal much resemble corresponding forms of platinum; though the palladious compounds (those of **Pd**$''$) are much more stable than the palladic salts (those of **Pd**^{IV}). With **iodides**, palladious chloride precipitates *palladious iodide*, PdI_2, black, a close separation of iodine from bromine and chlorine. The dark brown precipitate of *palladious sulphide* is **insoluble in ammonium sulphide,** soluble in nitro-hydrochloric acid, not in dilute nitric acid (accompanying **HgS** in the work of Group II.) Palladium is reduced by sulphurous acid, stannous and ferrous salts, and reduced to "sponge" by ignition on charcoal.

Molybdenum.

196. Molybdous compounds (those of **Mo**$''$) are not stable in soluble forms. Molybdic salts (containing **Mo**^{IV})—the chloride, sulphate, nitrate—are had in solution. Molybdic anhydride, $Mo^{VI}O_3$, representing molybdates as salts of H_2MoO_4, is but slightly soluble in water, and is non-volatile. The alkali metal molybdates are soluble in water, other molybdates insoluble. Solutions of alkali metal molybdates, with acids, give a precipitate of MoO_3, soluble in excess of the acid. Ammonium molybdate, with enough nitric acid to redissolve the molybdic anhydride, is a **Reagent** much used for **phosphoric acid**, giving a yellow precipitate called *ammonium phosphomolybdate* (of variable composition), soluble in ammonia and other alkalies, somewhat soluble in excess of phosphoric acid (hence the molybdate must be used in excess). *Sodium phosphomolybdate* is soluble in water, and precipitates ammonium from its salts; also, it precipitates the organic alkaloids and is used as a general reagent for these bodies. **Reducing agents**

give various colored products with molybdates—the most frequent being of blue color, intermediate oxides, molybdic molybdates. Fröhde's reagent for alkaloids is ammonium molybdate freshly dissolved in over 1,000 parts of sulphuric acid—this reagent giving certain colors with alkaloids and other reducing agents. A stronger solution of molybdate in concentrated sulphuric acid turns blue when heated to the vaporizing point of the sulphuric acid.

QUALITATIVE CHEMISTRY OF THE METALLOIDS AND ACIDS.

197. *The three elements, chlorine, bromine, and iodine,* differ from each other with a regular and progressive gradation, in many particulars, such as the atomic weight, the physical condition of the elements, the stability of their corresponding compounds, and the solubilities of their similar salts. The gradation is found both in the univalent series, and in the pentivalent series. These orderly differences are, in good part, shown in the following table:

Comparison of Chlorine, Bromine, and Iodine.

	Cl'	**Br'**	**I'**
Atomic weight:	35.5	80	127
Ordinary state:	Gas.	Volatile liquid.	Volatile solid.
Hydracids:	**HCl**, not decomposed by air.	**HBr**, slowly decomposed by air.	**HI**, readily decomposed by air.
Haloid salts:	Not decomposed by **Br** nor **I**.	Decomposed by **Cl**, not by **I**.	Decomposed by **Cl** and by **Br**.
Salts insoluble in water:	**$PbCl_2$** (slightly soluble). **$AgCl$**. **Hg_2Cl_2**.	**$PbBr_2$**. **$AgBr$**. **Hg_2Br_2**.	**PbI_2**. **AgI**. **Hg_2I_2** and **HgI_2**.
Silver salts, with **NH_4OH**:	Freely soluble.	Sparingly soluble.	Little soluble.
	Cl^V	**Br^V**	**I^V**
Oxacids:	**$HClO_3$**, very instable.	**$HBrO_3$**, moderately stable.	**HIO_3**, stable below 170° C.
Oxysalts:	All soluble in water; **$KClO_3$** only moderately soluble.	All soluble; those of First Group, sparingly.	All non-alkaline, insoluble or sparingly soluble.

198. CHLORINE is a greenish-yellow gas, suffocating to breathe, corrosive to organic tissues and fabrics, bleaching organic colors, and being chemically very active. It can be obtained by acting on hydrochloric acid (or on common salt and sulphuric acid) with some strong "oxidizing agent," when the **H** of the **HCl** enters into a new combination and the **Cl** is set free, thus:

$$2HCl + O \text{ (nascent)} = H_2O + ClCl$$

The following experiments are examples, identifying the free chlorine in each case, as advised in 199.

a. Treat **HCl**, or **NaCl** and H_2SO_4, with MnO_2, heating, as directed and explained in note under 100.

b. Make nitro-hydrochloric acid, as directed in 22, warm, and test for chlorine.

c. Treat **HCl** with $KClO_3$, as directed in 210, and test for chlorine.

199. *Free chlorine is characterized* by bleaching wet **litmus-paper**; by liberating iodine from **potassium iodide**, this being a very delicate test if fresh starch paste is first added to the iodide (225 *b*); and by changing a **ferrous salt** to ferric salt, so that ferricyanide is not longer precipitated blue (see 99 *b*). It does not color starch (distinction from bromine and iodine).

200. *Chlorine gas is dissolved* a little by water; very little if the water is hot. The solution, Chlorine Water, is pharmacopœial, and is used as a reagent, as mentioned in 22. By standing, even in perfectly close bottles, it loses value, the chlorine decomposing the water and uniting with its hydrogen, so that test-paper is reddened and no longer bleached by it. Chlorine water is made by delivering chlorine gas into water (note under 100). If Marsh's apparatus is used to generate and conduct the chlorine, heating the generator, some hydrochloric acid will be apt to go over with the chlorine, unless the gas is passed through a "wash bottle"; nevertheless the acid chlorine water may be used for most tests.

201. The chief **Acids containing Chlorine** are:
Hydrochloric acid, **HCl'**, forming chlorides.
Chloric acid, **$HCl^{V}O_3$**, forming chlorates.
Hypochlorous acid, **$HCl'O$**, forming hypochlorites.

Hydrochloric Acid.

202. Absolute hydrochloric acid (chlorhydric acid) is a colorless, caustic, suffocating gas; soluble in about twice its weight of water, so that its strongest permanent solution contains about 33 per cent. of acid (**HCl**). The U.S. P. "Hydrochloric Acid" ("muriatic acid"), specific gravity 1.16, has about 32 per cent. of acid; the reagent, of Fresenius' standard, sp. gr. 1.12, about 24 per cent. of acid. Even this solution, it will be observed, gives off gaseous acid (reddening litmus) on opening the bottle.

203. On adding **sulphuric acid** to chlorides (in solid state or concentrated solution) *hydrochloric acid* is formed, and will escape with a slow effervescence. In this way, using common sodium chloride, the acid is manufactured on the large scale. The change is a transposition of the metal of the chloride for half or the whole of the hydrogen of the sulphuric acid:

$$\mathbf{NaCl + H_2SO_4 = NaHSO_4 + HCl}$$
$$\mathbf{2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl}$$

But **Hg, Ag, Pb,** and **Sn** chlorides are decomposed with difficulty by sulphuric acid; so that, if these bases are present, the test by the gas is not so readily made.

204. The gas, generated as just mentioned, is identified as follows: (In common with other vaporous acids, it reddens wetted blue litmus-paper.) (If bromides are present, see **205.**)

(*a*) A drop of **silver nitrate** solution, on a glass rod, held in the mouth of the test-tube, is precipitated by the hydrochloric acid gas, as *silver chloride*, $AgCl$, white and curdy. A few drops of ammonium hydrate, in another test-tube, promptly dissolve the precipitate from the rod (a distinction from iodide); and now on adding a drop or two of nitric acid, enough to give the acid reaction to litmus-paper, the precipitate of $AgCl$ appears again,—evidence of chloride. (Compare, under Silver, 148.)

$$HCl + AgNO_3 = AgCl + HNO_3$$
$$2AgCl + 3NH_4OH = (AgCl)_2(NH_3)_3 + 3H_2O$$
$$(AgCl)_2(NH_3)_3 + 3HNO_3 = 2AgCl + 3NH_4NO_3$$

Mercurous nitrate solution is also precipitated by the gas, and concentrated solutions of **lead salts** (all the first group bases).

(*b*) The gas HCl, with the vapor, NH_3, arising from **ammonium hydrate** solution, forms a white cloud of ammonium chloride (in the solid state). Other volatile acids, however, to some extent give a white cloud of ammonium salts in this test.

205. Solutions of chlorides, and hydrochloric acid, are precipitated by **salts of First Group metals**; *the chlorides of other metals being soluble in water.** Of the reagents, calcium, ammonium, and ferric chlorides may be taken *for experiment*, writing equations with each. Ordinary common salt is apt to contain an appreciable proportion of sulphate. The precipitates are:

Silver chloride, $AgCl$, (as in the test of HCl gas, 204 *a*).
Mercurous chloride, Hg_2Cl_2, blackened by NH_4OH, see **Hg**, 153.
Lead chloride, $PbCl_2$, sparingly soluble in water, 144.

* **Transposition between two salts**: *On mixing solutions of any two salts capable of forming, by exchange of bases, a salt insoluble in the solvent present, the insoluble salt is produced and precipitated.* If lead sulphate is insoluble in water, the following change will occur and a precipitate appear as a result:

Lead nitrate + sodium *sulphate* = *lead sulphate* + sodium nitrate.

In presence of bromides, the tests by 204 cannot be relied on for chlorides, and, if *iodides* are present, these may be mistaken for chlorides unless the easy solubility of the silver precipitate in ammonium hydrate is assured. *If bromides have been found*, precipitate the solution with silver nitrate, wash the precipitate with water, digest with warm ammonium carbonate solution (or with very dilute ammonium hydrate), and slightly acidulate the filtered solution with nitric acid, when a precipitate gives evidence of chloride (in distinction from bromide or iodide). (See 197.)

206. Silver chloride is not decomposed by acids; Mercurous chloride is very slowly changed to mercuric salts by nitric acid; and in analysis of both these chlorides, to find their acid radicals, they are fused with sodium carbonate on charcoal, when the mass treated with water gives sodium chloride solution to be tested for the acid. In case of silver, the metallic mass, not dissolved by water, is now treated with nitric acid, when a solution is obtained to test for bases. The following equations represent this class of changes:

$$4AgCl + 2Na_2CO_3 + C = 4Ag + 4NaCl + 3CO_2$$

$$2Hg_2Cl_2 + 2Na_2CO_3 + C = 4Hg \text{ (vaporized)} + 4NaCl + 3CO_2$$

$$2PbCl_2 + 2Na_2CO_3 + C = 2Pb + 4NaCl + 3CO_2$$

Chloric Acid.

207. Chloric acid, $HClO_3$, is so instable as to be difficult of preparation and preservation, and is not at all in use. The only chlorate in use is *Potassium Chlorate* (U. S. P.), one of the least soluble chlorates, requiring 12 to 16 parts of cold water to dissolve it. (In alcohol it scarcely dissolves at all.)

*All the metallic chlorates are soluble in water.**

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* There are *three acids* whose salts, in common use, are all soluble in water, namely: Nitric, Chloric, and Acetic acids.

208. Though causing no precipitates in water solutions, *potassium chlorate* has very serious incompatibilities. *With any combustible material it makes an explosive mixture*, like gunpowder, only more violent (!), exploding when heated and very liable to explode in the mortar. It should be pulverized by itself, and any combustible material should be mixed with it either on paper or in some way devoid of pressure or concussion. A chlorate is an active oxidizing agent, more active than the nitre of gunpowder (the action of which is given in 237). $\mathbf{KClO_3}$ gives up $\mathbf{O_3}$, leaving $\mathbf{KCl}$: a method of preparing oxygen gas. When any oxidizable substance is brought in contact with a chlorate, as soon as the mixture is ignited a very rapid and condensed combustion takes place, the heated gases of which expand to their normal volume, as in case of most explosions. Of easily combustible substances, note charcoal, sulphur, sulphites, hyposulphites (thiosulphates), hypophosphites, reduced iron, sugar, tannic acid, and indeed all organic substances.

209. On decomposing a small fragment of chlorate, in solid, with **sulphuric acid**, chloric acid is not obtained intact, but gaseous products of greenish yellow color, with sharp detonation; the use of larger quantities giving violent explosion. The detonation and gas color are characteristic of chlorates. Further, it is distinctive, that chlorates give no precipitates with any bases, but, when ignited (on platinum foil), are reduced to chlorides, whose solutions precipitate first group bases.

210. Potassium chlorate and hydrochloric acid are much used together to furnish "euchlorine" and free chlorine, as an oxidizing agent. The action requires heating to start it. The results vary, but are represented by this equation:

$$\mathbf{2KClO_3 + 4HCl = 2KCl + Cl_2O_4 + 2Cl + 2H_2O}$$

Hypochlorous Acid.

211. Hypochlorous acid, $\mathbf{HClO}$, is very instable and is not in use. Most metals form hypochlorites, all easily decomposed. Combined hypochlorite-chloride of calcium, probably **$CaCl_2.Ca(ClO)_2$**, is in very extensive use, as "*Chlorinated Lime*," U.S.P., "Chloride of Lime," or "Bleaching Powder"—for bleaching cloth, paper, and other fabrics, and as a disinfectant. A corresponding sodium hypochlorite-chloride, **NaCl.NaClO**, in solution, is pharmacopœial as "*Solution of Chlorinated Soda*," "Labarraque's Disinfecting Liquid." The chlorinated lime is manufactured by passing chlorine into slaked lime. The pharmacopœia requires that it shall yield not less than 25 per cent. of free chlorine, on which its value wholly rests; but it loses chlorine so rapidly in the air that, in the dispensing trade, it is often nearly valueless.*

The carbonic anhydride of the air liberates chlorine from the chlorinated bases, perhaps as follows:

$$CaCl_2.Ca(ClO)_2 + 2CO_2 = 2CaCO_3 + 4Cl$$

212. *The chlorinated compounds are recognized* by their strong, characteristic, chlorous odor; by spontaneous evolution of chlorine gas, giving tests of the latter; by dissolving in water, and the solution both giving reactions of a chloride and bleaching litmus. *The oxidizing power* of chlorinated compounds is very active, and is the same as that of chlorine gas in solution with free alkaline hydrate.

213. BROMINE is in use as a very volatile liquid, giving off vapor so fast at atmospheric temperatures that it is confined with difficulty, even in small bottles, and boiling at 47° C. (117° F.) The vapor is brown-red, intensely caustic and suffocating, with an odor somewhat resembling chlorine. It is *soluble* in 33 parts of water (bromine water), freely soluble in water solutions of most bromides, and in alcohol, ether, chloroform, and carbon disulphide,—its solutions having an orange-yellow to brownish-yellow color. The use of carbon disulphide, or chloroform solution, in analysis, is given in 217. Bromine colors starch yellow.

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* See U. S. P. quantitative test, requiring full oxidation of a certain quantity of ferrous salt, by a stated quantity of the chlorinated lime.

It dissolves colorless in alkali hydrate solutions, by forming bromide and bromate—the first step in one method of manufacturing potassium and sodium bromide:

$$6Br + 6KOH = 5KBr + KBrO_3 + 3H_2O$$

As to the relative chemical force of bromine, see 197.

214. The Acids of Bromine:

Hydrobromic acid, HBr', representing bromides.
Bromic acid, $HBr^{v}O_3$, representing bromates.
Hypobromous acid, $HBr'O$, representing hypobromites.

Hydrobromic Acid.

215. Pure hydrobromic acid, **HBr**, is gaseous at common temperatures, but is dissolved and pretty well retained by water, a ten per cent. water solution being now in medicinal use. Potassium and ammonium *bromides* are pharmacopœial, sodium bromide is used in medicine, and bromide of iron is in commerce as a form more convenient to handle than free bromine.

216. Hydrobromic acid is formed by transposition when dilute **sulphuric acid**, or excess of hydrochloric acid, is added to a bromide:

$$2KBr + H_2SO_4 = K_2SO_4 + 2HBr$$

Concentrated sulphuric acid liberates some free bromine, and **Chlorine water** does this completely. Hydrobromic acid, in the air, very slowly furnishes free bromine. Bromine is liberated at once by manganese dioxide with sulphuric acid, as stated in paragraph 100, where a corresponding equation for iodine is given.

217. *The test of free bromine, as evidence of bromides,* is made as follows: (*a*) To the concentrated solution, or solid substance, or residue by evaporation, in a test-tube, add good **Chlorine water**, then dilute and add about a cubic centimeter ($\frac{1}{4}$ fluid drachm) of **carbon disulphide** (or chloroform), agitate well, and set aside till the carbon disulphide (or chloroform) has settled into a clear layer below. A yellow color, or brownish yellow if the bromine is very abundant, indicates bromine. The test is but moderately delicate.

(*b*) Add fresh **starch paste**, then gradually add good **Chlorine water**, when a yellow color indicates bromine (not a delicate test).

218. *If iodides are present,* only a test for iodine will be obtained by *a* or *b*, so that it is necessary either to *remove all the iodine* or, what is more satisfactory, to *oxidize it to iodic acid* before a test for bromine can be made. *To remove the iodine:* (1) Add sufficient carbon disulphide, and then chlorine water, by drops, as long as the addition of the chlorine continues to deepen the violet tint of iodine. Remove the violet carbon disulphide with a small mouth pipette, or with a little siphon made of small glass tubing and first filled with water; add fresh carbon disulphide and continue the gradual addition of chlorine. When the violet color is no longer obtained, with fresh carbon disulphide, or chloroform, continue for the bromine. (2) If iodides are abundant, the most of the iodine can be precipitated by adding copper sulphate solution with ferrous sulphate solution (228); when the filtrate must be treated as directed in (1). *To oxidize the iodine to iodic acid:* Generate chlorine gas, in a tubulated flask, with manganese dioxide and hydrochloric acid (100), and conduct the chlorine into the solution, till the iodine color disappears, when the bromine test can be obtained. Strong chlorine, itself, may color carbon disulphide yellow (liberating sulphur). To avoid this, use chloroform.

219. *Bromides in solution, are precipitated* with—

Lead salts, as **$PbBr_2$**, less soluble in water than lead chloride.

Silver salts, as **$AgBr$**, less sol. in **NH_4OH** than silver chloride, not dissolved by dilute nitric acid.
Mercurous salts, as **Hg_2Br_2**, yellowish white.

See Comparison with Chlorides and Bromides, 197.

220. IODINE, as a free element, is an article of considerable commerce, obtained from the iodides of kelp or sea-weed ash (set free as stated in 100) and from the iodates of Peruvian nitre. The U. S. P. has "Iodine," and a "Tincture," "Compound Tincture," and "Compound Solution" of iodine, the last two preparations containing potassium iodide. Iodine is used for the manufacture of iodides.

221. Iodine is in lustrous, iron-gray scales, subliming very slightly at common temperatures, melting at 107° C. (224° F.), and boiling at 180° C. (356° F.), the vapor having a bright violet color. It is slightly soluble in water, freely *soluble* in water solutions of iodides (including **HI**), and in alcohol, ether, chloroform, carbon disulphide, and glycerine, the iodine in all these solutions remaining chemically free, retaining its brownish-red color, and staining the skin, and turning starch blue. It dissolves with chemical combination, and loss of color, in solutions of alkali hydrates, forming, with fixed alkali hydrates, iodide, and iodate, as follows:

$$6I + 6KOH = 5KI + KIO_3 + 3H_2O$$

This is the first step in the U. S. P. preparation of iodide of potassium; and, with use of ammonium hydrate (water or spirit of ammonia), it is the chief reaction in preparation of the assumed "*colorless tinctures of iodine.*" These are solutions of ammonium iodide (U. S. P.) and iodate, liable to contain a dark precipitate of nitrogen iodides (**NI_3**, or **NHI_2**, or **NH_2I**), explosive, also liable to contain iodoform if alcohol is present. Sulphites, and hyposulphites, and carbolic acid, are likewise used to furnish so-called colorless iodine solutions, but no solution holding free iodine is colorless, or applicable to the skin without staining it. The action of a sulphite upon free iodine is an example of the action of reducing agents generally, including hydrosulphuric acid and arsenious acid:

$$2I + H_2O + Na_2SO_3 = 2HI + Na_2SO_4$$
$$2I + H_2S = 2H_2I + S$$

The blue iodized starch is decolored by the above-mentioned and other alkali hydrates and reducing agents,* no compound of iodine giving the blue test with starch.

222. **The Acids of Iodine** here given for study are:

Hydriodic acid, HI', forming iodides.
Iodic " $HI^{V}O_3$, " iodates.

Hydriodic Acid.

223. Absolute hydriodic acid, **HI**, is gaseous, but dissolves abundantly in water. Both the gas and the solution are colorless when undecomposed, but begin at once to turn red-brown in the air by separation of free iodine: $2HI + O = H_2O + 2I$. Hydriodic acid is seldom used. The *iodides* are in extensive use: those of Potassium, Ammonium, Arsenic, Sulphur, and Lead are pharmacopœial,—and potassium iodide is largely used in photography.

224. Hydriodic acid is formed from iodides by transposition, with **dilute sulphuric acid**, and with excess of **hydrochloric acid**, and **hydrobromic acid**.

$$2KI + H_2SO_4 = K_2SO_4 + 2HI$$

Sulphuric acid not diluted, acting as an oxidizing agent, separates some free iodine, as follows:

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* The student may *experiment* in preparation of the iodine compounds made as "colorless tinctures," and in decoloring the blue iodized starch, using any form of free iodine at hand, with alkalies and reducing agents as mentioned in the text.

$$2KI + H_2SO_4 = K_2SO_4 + H_2O + 2I$$

Iodides of silver, lead, mercury, and tin, are transposed with difficulty by sulphuric acid; more easily by hydrochloric acid.

225. In *testing for iodides*, the test of liberated iodine, by **carbon disulphide** (*a*), or **starch paste** (*b*), is both distinctive and delicate. **Chlorine water** liberates the iodine instantly, and, when sparingly added, serves the best. **Sulphuric acid** liberates **HI**, and, by action of the air, the free iodine is gradually obtained.

a. Add to a little of the material, solid or dissolved, but not alkaline to test-paper, in a test-tube, about a cubic centimeter (¼ f. drachm) of carbon disulphide (or chloroform). Then add a little good chlorine water, shake, and leave the solvent time to settle, when the under layer will show the bright violet color of the iodine, if iodides were present.

b. To the material, solid or dissolved, add fresh starch paste (made by boiling a little bit of starch with water), and, when cool, add a little chlorine water. Iodine, in evidence of iodides, is shown by a deep blue to violet-blue color, the *iodized starch*, an intimate mixture by adhesion, not a chemical compound.

Excess of free chlorine, more readily at the instant of its liberation, oxidizes free iodine to iodic acid, preventing tests *a* and *b*, and used to avoid interference of iodine with the test for bromine, as given in 218.

226. *If iodates are present* with iodides, any addition of dilute sulphuric acid, or even of weak acids, causes immediate separation of free iodine, instead of hydriodic acid, see 232. Indeed, *oxidizing agents* generally, readily liberate iodine.*

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* *Try oxidizing agents* with potassium iodide, in acidulate solution, for separation of iodine, recognized by its color alone. When more iodine is liberated than the solution of iodide can dissolve, as in concentrated solution with excess of the oxidizing agent, a precipitate of iodine may be obtained. Any of the following may be used: nitro-hydrochloric acid, nitric acid with heat, manganese dioxide (100) with an acid, chromates with an acid, permanganate with an acid, iodate with an acid, nitrite with an acid.

227. *Solutions of iodides give precipitates* as follows:

With Lead	salts,	PbI_2,	yellow, very slightly soluble in water.
" Silver	"	AgI,	yellowish-white, but very slightly dissolved by NH_4OH (separation from chloride).
" Mercurous	"	Hg_2I_2,	green to yellow, liable to immediate change to Hg, dark gray, and HgI_2, yellow-red, dissolving in excess of precipitant.
" Mercuric	"	HgI_2,	yellow to red, soluble in excess of KI, as potassio mercuric iodide, $(KI)_2HgI_2$.

228. *Copper salts with reducing agents,* as cupric sulphate with either ferrous sulphate or sulphurous acid, precipitate *cuprous iodide,* Cu_2I_2 brownish-white:

$$4KI + 2CuSO_4 + H_2SO_3 + H_2O = Cu_2I_2 + 2K_2SO_4 + H_2SO_4 + 2HI$$

A separation from bromine, not quite complete (218). Palladium chloride separates iodides from bromides and chlorides, as stated more fully in 195.

229. Iodides of alkali metals, and of lead and silver, melt without decomposing. Mercury iodides sublime with little decomposition.

Iodic Acid.

230. Iodic acid, HIO_3, is a solid, white, crystallizable, not volatile, freely soluble in water. Neither the acid nor its salts have been applied to the uses of life. Iodates occur in course of manufacture of iodides, and are sometimes present as impurities in the iodides of commerce.

231. Iodates, in solution, are precipitated by **barium salts,**

silver salts, and **lead salts.** Only the alkali metal iodates are freely soluble in water,—a marked distinction from chlorates and bromates, as noted in the comparison at 197. Potassium iodate is insoluble in alcohol (a separation from iodide).

232. **Reducing agents** separate iodine from iodic acid, and then, if applied in excess, mostly bring the iodine into combination again, as iodide or hydriodic acid. Thus:

$HIO_3 + 3H_2S = HI + 3H_2O + 3S$, *and at once:*
$HIO_3 + 5HI = 6I + 3H_2O$. *Again:*
$2I + H_2S = 2HI + S$.

Sulphurous acid with starch, added short of saturation, makes a delicate test for iodic acid. *The presence of iodate* in an article of potassium iodide is quickly shown by the separation of iodine on adding a dilute acid not an oxidizing agent, as tartaric acid or oxalic acid. The iodic acid test for morphia depends on the reducing power of the alkaloid.

233. **NITROGEN,** when free, does not enter into combination with other free elements, at any temperature, unless these are in the nascent state. But the compounds of nitrogen are generally changed, the one to another, with comparative ease; thus, ammonia, $N'''H_3$, is pretty easily oxidized to nitric acid, $HN^{V}O_3$, and nitric acid is readily reduced to nitrous acid, $HN'''O_2$, and to ammonia, again (40). The decomposition of the organic compounds of nitrogen gives rise to ammonia, to cyanogen, and to acids of nitrogen; seldom to free nitrogen.

234. **The compounds of nitrogen** given for study in this work are these:

Ammonia,	$N'''H_3$,	forming	ammonium salts (37).
Nitric acid,	$HN^{V}O_3$,	"	nitrates (235).
Nitrous "	$HN'''O_2$,	"	nitrites (242).
Cyanogen,	$(C^{IV}N''')'$	"	several acids (247).

Nitric Acid.

235. Absolute nitric acid, $\mathbf{HNO_3}$, is liquid, of specific gravity 1.58 (at 15° C.), very difficult to preserve without some decomposition, and scarcely an article of commerce. U. S. P. "Nitric Acid," sp. gr. 1.42, 70 per cent. of $\mathbf{HNO_3}$, is a stable liquid, distilling with little alteration of strength. The reagent, Fresenius' standard, sp. gr. 1.2, has about 35 per cent. of $\mathbf{HNO_3}$. "Aqua fortis" is a synonym still applied to certain grades of the acid in commerce.

The nitrates used as sources of the acid, and the nitrates in explosive agents, and fertilizers, are potassium nitrate, "nitre" or "saltpetre," and sodium nitrate, "Peruvian nitre" or "Chili saltpetre."

236. Nitric acid is obtained from either of the nitrates just mentioned by transposition with sulphuric acid, not diluted:

$$\mathbf{KNO_3 + H_2SO_4 = KHSO_4 + HNO_3}$$

In a hot mixture, the nitric acid rises as a gas, very slowly and without effervescence, colorless, or, from some decomposition, slightly reddish, turning litmus red, and giving an acrid characteristic odor.

237. *Nitric acid is identified* by color products of its *decomposition,* no precipitates being made by it. The acid decomposes readily, in accordance with the feeble chemical force of nitrogen, mentioned in 233, the action of a reducing agent being all that is needed. *The action of nitrates in explosions* is due to their decomposition by reducing agents. In Gunpowder, the potassium nitrate is acted on by charcoal and sulphur. *Any combustible substance* is, of course, a reducing agent. Drop potassium nitrate upon burning charcoal, and the combustion, the oxidation, of the carbon is quickened to explosive rapidity. A grain of nitre holds about a cubic inch and a third of oxygen, as much as six cubic inches of the air. Dangerous explosion may occur from heating, pounding, or triturating nitrates with any easily oxidizable substances, as sulphur, charcoal, cyanides, hypophosphites, sugar, tannin, and most organic compounds. With small quantities, not confined, the action is mere detonation or deflagration. (Compare, Chlorates, 208.)

The reducing agents most used in testing for nitric acid are *ferrous sulphate* for "the brown ring test" (238, *a*), and the same reagent or *metallic copper*, for the brown vapor test (238, *b*).

238, *a*. Take **sulphuric acid** to a quarter of an inch in depth in the test-tube; add without shaking a nearly equal volume of **ferrous sulphate** solution, and cool the liquid; then add slowly of the solution to be tested for nitric acid, slightly tapping the test-tube on the side, but not shaking. The "*brown ring*," a layer of brown to black, or reddish, liquid, between the sulphuric acid below and the solution above, gives evidence of nitric acid (or of nitrous acid).

$$2KNO_3 + 4H_2SO_4 + 10FeSO_4 = K_2SO_4 + 3Fe_2(SO_4)_3 + 4H_2O + 2(FeSO_4)_2NO$$

This equation may be studied in the following steps:

(1) Transposition: $2KNO_3 + H_2SO_4 = K_2SO_4 + 2HNO_3$

(2) *Two molecules of nitric acid furnish three atoms of oxygen* (half the whole), leaving nitric oxide and water:

$$2HNO_3 = H_2O + 2NO + 3O$$

(3) $3O + 6FeSO_4 + 3H_2SO_4 = 3Fe_2(SO_4)_3 + 3H_2O$

(4) $2NO + 4FeSO_4 = 2(FeSO_4)_2NO$ (an instable compound).

b. To a solution to be tested for nitrate add a bit of **copper,** in wire or turnings (or solid ferrous sulphate), and **sulphuric acid,** and heat. Reddish-brown vapors indicate a nitrate.

$$2KNO_3 + 4H_2SO_4 + 3Cu = K_2SO_4 + 3CuSO_4 + 4H_2O + 2NO$$

The brown vapors are due to the formation of nitric oxide gas, NO, by action of the chemicals, colorless, and the oxidation of this colorless compound, by action of the air, to higher oxides of nitrogen, N_2O_3 and N_2O_4, colored.

239. **Magnesium** (wire or ribbon), in solution acidulated with phosphoric acid, reduces nitric acid to ammonia (233), which may be tested for with potassio mercuric iodide (156) and potassium hydrate.

240. **Phenol**, or the best Carbolic Acid, C_6H_6O, gives a deep red-brown color with nitric acid, or a nitrate and sulphuric acid, by formation of a nitrophenol (picric acid), $C_6H_3(NO_2)_3O$.

241. *All the normal nitrates are soluble in water*, so that nitric acid is not liable to precipitation.

Nitrous Acid.

242. This acid, HNO_2, is hardly known as a free acid, in pure state or in solution, owing to its extreme instability. Potassium nitrite is in commerce for chemical uses. Nitrites are not seldom present, as impurities, in a small proportion, in the nitrates of potassium, and silver, of commerce. If a nitrate in preparation is too strongly heated, some nitrite is formed.

243. Nitrites, in solid or solution, treated with **acids**, dilute sulphuric or even dilute acetic acid, evolve *brown nitrous vapors* abundantly. With acetic acid, this is a test for nitrites, and a distinction from nitrates. In this change, the elements of nitrous acid so divide as to produce nitric acid and nitric oxide :

$$3HNO_2 = HNO_3 + 2NO + H_2O$$
$$6KNO_2 + 3H_2SO_4 = 3K_2SO_4 + 2HNO_3 + 4NO + 2H_2O$$

244. *In the "brown ring" test* (238, *a*) nitrites give the same appearance as nitrates. If *acetic acid* be substituted for sulphuric acid in this test, the "brown ring" is nevertheless obtained with nitrites (a distinction from nitrates).

245. Nitrites, acidulated with acetic acid, or very dilute sulphuric acid, instantly *liberate iodine from iodide of potassium*, a delicate test, distinguishing nitrites from nitrates.

The reactions given in 244 and 245 are among many instances of the *oxidizing power* of nitrites, but in other instances they manifest *reducing power*, being oxidized to nitrates. As an example of deoxidation, **permanganate of potassium** solution is decolored by acidulated nitrite solution.

246. *The nitrites are all soluble in water*,—silver nitrite somewhat sparingly soluble.

247. CYANOGEN, $(C^{iv}N''')'$ or Cy', is a poisonous gas, soluble in water, and a constituent of some important **acids**, of which the following will be given here:

Hydrocyanic	acid,	$HC^{iv}N'''$ or HCy,	forming	cyanides.
Hydroferrocyanic	"	$H_4Fe''Cy_6$,	"	ferrocyanides.
Hydroferricyanic	"	$H_3Fe'''Cy_6$,	"	ferricyanides.
Sulphocyanic	"	$HCyS$,	"	sulphocyanates.

Hydrocyanic Acid.

248. Hydrocyanic Acid, "Prussic Acid," **HCy**, when absolute, is a colorless liquid, boiling at 27° C. (81° F.), and soluble in water in all proportions. U. S. P. "Hydrocyanic Acid" is a water solution, 2 per cent. being acid.* Oil of Bitter Almonds frequently contains hydrocyanic acid, which is formed along with it, from amygdalin, a constituent of most plants of the almond family. Cyanide of potassium is used in various arts, especially in photography. It gives off some hydrocyanic acid, and by standing acquires potassium hydrate and carbonate. Silver cyanide is pharmacopœial for the preparation of hydrocyanic acid by a ready method.

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* The vapor, if not greatly diluted with air, is a quick poison, by inhalation. Antidotes, inhalation of ammonia; of chlorine, cautiously.

249. Hydrocyanic acid is formed from cyanides by transposition with even feeble acids and when very dilute. It is formed from potassium ferrocyanide by action of hot sulphuric acid (one method of preparation, U. S. P.)

The gas, **HCy**, rises readily—with effervescence if formed in concentrated solutions—having a characteristic odor (to be tested with caution when abundant), and, with **silver nitrate** solution wetting a glass-rod, giving a white precipitate, **AgCy**, having nearly the same solubilities as chloride of silver.

250. A delicate and distinguishing test is *the formation of sulphocyanate*, as follows: Warm the material, in an evaporating dish, with a few drops of **ammonium sulphide**, till the mixture is free from the sulphide. (Filter if there is any residue or precipitate.) Slightly acidulate the solution, with hydrochloric acid (which should not liberate H_2S), and add a drop of solution of **ferric chloride**. A blood-red solution, decolored by solution of mercuric chloride, gives evidence of hydrocyanic acid or its salts (257).

251. Cyanides of alkali metals, alkaline earth metals, and mercuric cyanide, are **soluble** in water, most others insoluble. Many of the precipitated cyanides dissolve in solutions of alkali cyanides, soluble **double cyanides** being formed. Thus, a precipitate of cupric cyanide, $CuCy_2$, formed by adding potassium cyanide, by a further addition of this solution dissolves, as potassio copper cyanide, $(KCy)_2CuCy_2$. This double cyanide, like others of its class, treated with dilute sulphuric acid, decomposes into K_2SO_4, $CuSO_4$, and $4HCy$.

Another class of double cyanides act differently with dilute sulphuric acid and other acids: If a ferrous salt be precipitated by potassium cyanide, and then the precipitate, $FeCy_2$, dissolved by adding more of the reagent, a double salt is formed in solution, $(KCy)_4FeCy_2$, *potassium ferrous cyanide*. Adding dilute sulphuric acid to this, K_2SO_4 and $(HCy)_4FeCy_2$ are formed. The compound last given is found to act as a tetrabasic acid, $\mathbf{H_4(FeCy_6)^{IV}}$, forming stable salts with bases generally, and is termed hydroferrocyanic acid. The potassium salt of this acid, placed above as a double cyanide, is potassium ferrocyanide, $\mathbf{K_4FeCy_6}$, a simple salt of the acid radical, $\mathbf{(FeCy_6)^{IV}}$. Cobalt, manganese, and chromium, like iron, enter into acid radicals with cyanogen, forming cobalticyanides, manganicyanides, etc. This class of double cyanides are transposed by dilute alkalies. We have, then,

(1) Double cyanides from which dilute acids remove both the metals, forming hydrocyanic acid. Not decomposed by alkalies. Example: $\mathbf{(KCy)_2CuCy_2}$.

(2) Double cyanides from which dilute acids remove one of the metals, forming an acid holding the other metal in its radical. Transposed by dilute alkalies.* Example: $\mathbf{(KCy)_4FeCy_2}$, or $\mathbf{K_4FeCy_6}$.

252. A test for hydrocyanic acid, *by formation of ferrocyanide*, is as follows: To the material, add **potassium hydrate** and **ferrous sulphate**, and warm a short time, then acidulate, and add **ferric chloride**, when the formation of prussian blue shows that cyanide was present.

Hydroferrocyanic Acid.

253. The free acid, $\mathbf{H_4FeCy_6}$, is not used. Its commercial salts are *Ferrocyanide of Potassium*, "Yellow Prussiate of Potash," and *Ferric Ferrocyanide*, "Prussian Blue."

254. **The Ferrocyanides** of metals of the alkalies and alkaline earths are **soluble in water** (that of barium sparingly); of other metals insoluble in water. The following are some of the **ferrocyanides precipitated by adding potassium ferrocyanide:**

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* $\mathbf{Fe_4(FeCy_6)_3 + 12KOH = 2Fe_2(OH)_6 + 3K_4FeCy_6}$

With	**Bismuth**	salts,	$Bi_4(FeCy_6)_3$,	white.
	Copper	"	Cu_2FeCy_6,	red-brown.
	Ferrous	"	$K_2FeFeCy_6$,	whitish-blue.
	Ferric	"	$Fe_4(FeCy_6)_3$,	"Prussian Blue."
	Lead	"	Pb_2FeCy_6,	white.
	Manganese	"	Mn_2FeCy_6,	white, sol. by **HCl.**
	Silver	"	Ag_4FeCy_6,	white, turning bluish.
	Zinc	"	Zn_2FeCy_6,	white, gelatinous.

The precipitates are transposed by alkaline hydrates, are not formed in alkaline solutions, but are unchanged by dilute acids.

Hydroferricyanic Acid.

255. The ferricyanide in use is the potassium salt, K_3FeCy_6, "Red Prussiate of Potash." It is made by the oxidizing action of chlorine, or other like agent, upon ferrocyanide:

$$K_4FeCy_6 + Cl = K_3FeCy_6 + KCl$$

Reducing agents reverse this change.

256. The Ferricyanides are mostly insoluble, or sparingly soluble, in water, except those of the alkali and alkaline earth metals. The following are some of the precipitates obtained:

With	**Bismuth**	salts,	$BiFeCy_6$,	light brown.
	Copper	"	$Cu_3(FeCy_6)_2$	yellow-green.
	Ferrous	"	$Fe_3(FeCy_6)_2$,	"Turnbull's Blue."
	Ferric	"	no precipitate,	greenish solution.
	Lead	"	no precipitate,	except in conc. sol.
	Manganese	"	$Mn_3(FeCy_6)_2$,	brown.
	Silver	"	Ag_3FeCy_6,	red-brown.
	Zinc	"	$Zn_3(FeCy_6)_2$,	orange.

The precipitates are transposed by alkalies, but are formed in neutral or acidulated solutions.

Sulphocyanic Acid.

257. This acid, **$HCyS$**, is considered a sulphur acid, corresponding to the oxacid, **$HCyO$**, cyanic acid. It is, however, sometimes stated as a hydracid (hydrosulphocyanic), and its salts termed sulphocyanides. The salt used is Potassium Sulphocyanate, **$KCyS$**. The sulphocyanates of the alkali metals, alkaline earth metals, and those of iron, manganese, zinc, and cobalt, are **soluble in water.** The following are some characteristic **sulphocyanates**, as formed by solutions:

With	**Cobalt**	salts,	very concentrated, a *blue color*, **$Co(CyS)_2$**.
	Copper	"	concentrated, a black precip., **$Cu(CyS)_2$**, quickly becoming **$Cu_2(CyS)_2$**, white.
	Ferrous	"	no precipitate or color.
	Ferric	"	blood-red solution, **$Fe_2(CyS)_6$**, decolored by **$HgCl_2$** (distinction from acetic acid).
	Lead	"	**$Pb(CyS)_2$**, yellowish, cryst., slow pre.
	Mercurous	"	**$Hg_2(CyS)_2$**, white, used in "Pharaoh's serpents," swells when ignited, giving poisonous gases.
	Silver	"	**$AgCyS$**, white.

Alkalies decompose, but dilute acids do not change, sulphocyanates.

258. CARBON is an infusible, non-volatile solid, existing free in the varieties of Coal and in the Diamond, and in combination with other elements in all the Organic substances. It is left free, as charcoal, on the partial combustion of any organic compound. It oxidizes rapidly at the temperature of ignition, in ordinary combustion, but at atmospheric temperatures it is little affected by oxidizing agents, or by solvents.

259. The Acids containing Carbon, given for study in this work, are the following:

Carbonic Acid, $H_2C^{IV}O_3$,[*] forming carbonates.
$C^{IV}O_2$, carbonic anhydride, carbon dioxide, or carbonic acid gas.
Oxalic " $H_2C_2^{VI}O_4$,[†] forming oxalates.
The Cyanogen Acids, named in 247.
Acetic Acid, $H(C_2H_3O_2)'$, forming acetates.

Carbonic Acid.

260. Carbonic acid, H_2CO_3, is not known as such, but is represented by its salts, the carbonates. The anhydride, CO_2, styled carbonic acid in common language, is exhaled in the breath, formed in common combustion, and constitutes a small proportion of the atmosphere, indispensable to plants. **The Carbonates** of various bases are extensively in use. Normal Sodium Carbonate, crystallized, $Na_2CO_3 10H_2O$, is known as "soda" and "sal soda." Sodium Acid Carbonate, $NaHCO_3$, the "Bicarbonate of Sodium" U. S. P., is sold as "soda," or "saleratus," for bread-making. The "soda water," dispensed with syrups as a summer drink, is water saturated under pressure with carbon dioxide, usually obtained by action of dilute sulphuric acid upon marble dust. Aluminium, chromium and ferricum, antimony and tin, do not form carbonates; some other metals form only basic carbonates.

261. In analysis, carbonates are distinguished by the *sudden effervescence*—the escape of CO_2—on adding almost **any acid.** For this test, sulphuric acid should be diluted. Effervescence by adding acetic acid distinguishes carbonates from oxalates. The escaping gas is nearly odorless, quite colorless, and passed into solution of **calcium hydrate**, renders it turbid by precipita-

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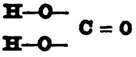
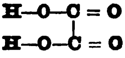
[*] Graphical formula:



$$\begin{array}{l} H{-}O{-} \\ \\ H{-}O{-} \end{array} C = O$$

[†] Graphical formula:



$$\begin{array}{l} H{-}O{-}C = O \\ \phantom{H{-}O{-}}| \\ H{-}O{-}C = O \end{array}$$

(Compare 19, Fe.)

tion of $CaCO_3$, *calcium carbonate* (the same substance as marble, limestone, "whiting," chalk). *Breathing* into the same reagent gives the same precipitate. Also, the gas, in barium hydrate solution, precipitates barium carbonate, and in basic lead acetate solution, or ammoniacal lead acetate solution, precipitates lead carbonate. But carbonic acid gas does not precipitate solutions of calcium salts, lead normal salts, or normal salts of any bases, owing to the easy decomposition of carbonates by nearly all acids.* Solutions of acid carbonates give up their excess of CO_2 on boiling.

262. The only **carbonates soluble in water** are those of the alkali bases, and solutions of these *carbonates cause precipitation in solutions of all non-alkali bases.*† The following are **the precipitates, by carbonates, with ordinary bases:**

With Barium	salts,	*barium normal carbonate,*	$BaCO_3$.
Calcium	"	*calcium* " "	$CaCO_3$.
Magnesium	"	*magn. basic* "	$Mg_4(CO_3)_3(OH)_2$.
Zinc	"	*zinc* " "	$Zn_5(CO_3)_2(OH)_6$.
Aluminium	"	*aluminium hydrate,*	$Al_2(OH)_6$.
Ferric	"	*ferric* "	$Fe_2(OH)_6$.
Ferrous	"	*ferrous carbonate,*	$FeCO_3$.
Manganous	"	*manganous carbonate,*	$MnCO_3$.
Chromic	"	*chromic hydrate,*	$Cr_2(OH)_6$.
Copper	"	*copper basic salts.*	
Bismuth	"	*bismuth basic carbonate,*	$Bi_2O_2CO_3$.
Lead	"	*lead* " "	$Pb_3(CO_3)_2(OH)_2$.
Silver	"	*silver carbonate,*	Ag_2CO_3.

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* That is to say, the change represented by this equation cannot occur:

$$CaCl_2 + CO_2 + H_2O = CaCO_3 + 2HCl$$

The [illegible]nge being complete, to take up all free hydrochloric acid.

$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2$$

† See Note under 205.

263. *On ignition*, the normal carbonates of potassium and sodium are not decomposed; the carbonates of barium, strontium, and calcium are slowly decomposed, leaving oxides (so that the remaining mass changes moistened red litmus-paper blue); the carbonates of other non-alkaline metals are readily decomposed, leaving oxides.

Oxalic Acid.

264. Oxalic acid is in commerce in white crystals, $H_2C_2O_4.2H_2O$, resembling magnesium sulphate, scarcely at all volatile without decomposition.

265. The acid can be formed by treating oxalates with dilute sulphuric acid, or with hydrochloric acid (equation in 267), but concentrated **sulphuric acid** with a little heat breaks it up, causing effervescence of carbon dioxide and monoxide:

$$H_2C_2O_4 = H_2O + CO_2 + CO$$

Acetic acid causes no effervescence (difference from carbonates).

266. The oxalates of the bases of the alkalies are **soluble in water**; those of most other metals are insoluble, or sparingly soluble. That is to say (note under 205) *solutions of non-alkali bases are precipitated by oxalates. Magnesium* oxalate is sparingly soluble, so that it is separated from the calcium oxalate precipitate by much water washing. *Chromic* oxalate dissolves freely in water. *Ferric* oxalate is somewhat soluble in water, and easily soluble in free oxalic acid. *Calcium* oxalate (the "oxalate of lime") is quite perfectly precipitated (see 53, note).

267. *The oxalates are transposed* by hydrochloric acid (separation from sulphates); not by acetic acid (separation from most of the phosphates).

$$CaC_2O_4 + 2HCl = CaCl_2 + H_2C_2O_4$$

268. Oxalic acid is a *reducing agent*, being oxidized to carbonic anhydride and water:

$$H_2C_2O_4 + O = H_2O + 2CO_2$$

In this way it precipitates gold (191), and decolors acidulated solution of permanganate:

$$2KMnO_4 + 5H_2C_2O_4 + 6HCl = 2MnCl_2 + 8H_2O + 10CO_2 + 2KCl$$

269. *By ignition in the air*, calcium oxalate is changed first to carbonate (effervescing with acetic acid), then, slowly, to oxide (turning litmus-paper blue). Silver oxalate decomposes suddenly, with a slight detonation.

Acetic Acid.

270. Absolute acetic acid, $HC_2H_3O_2$, sold as "Glacial Acetic Acid," is solid below 16° C.; vaporous liquid above this temperature. "Acetic Acid," U. S. P., the same strength as the reagent, has a specific gravity of 1.04, being about 30 per cent. of absolute acid. Vinegar has three to five per cent. of acetic acid, to which its sensible properties are chiefly due. The acetates of potassium, zinc, and lead are pharmacopœial.

271. The stronger mineral acids (as H_2SO_4) transpose acetates, forming *acetic acid*, which, in concentrated or hot solution, rises rapidly, giving the pungent odor of hot vinegar, and reddening litmus:

$$2NaC_2H_3O_2 + H_2SO_4 = Na_2SO_4 + 2HC_2H_3O_2$$

On warming an acetate with sulphuric acid and alcohol, *ethyl acetate* or "acetic ether," $C_2H_5C_2H_3O_2$, is formed, recognized by its penetrating, agreeable odor.

272. *The acetates are all soluble in water;* mercurous and argentic acetates, sparingly soluble. **Ferric salts,** with acetates, give a red solution of *ferric acetate*, not decolored by mercuric chloride (distinction from sulphocyanate), precipitated on long boiling, as basic ferric acetate, red-brown.

273. **SULPHUR** is a well-known solid, light-yellow, brittle, melting at 111° C. (232° F.), vaporizing at 445° C. (836° F.), burning in the air to sulphurous anhydride when ignited, insoluble in water, soluble in carbon disulphide, dissolved by chemical union in hot solutions of alkaline hydrates, slowly oxidized by hot nitric acid to sulphuric acid. It is sold as Roll Sulphur or "Brimstone"; "Sublimed Sulphur," U. S. P., or "Flowers of Sulphur," and "Precipitated Sulphur," U. S. P. "Milk of Sulphur" (sulphur lotum) is a name sometimes applied to Precipitated Sulphur, more often when the article contains calcium sulphate in large proportion, owing to precipitation by sulphuric instead of hydrochloric acid. Precipitated Sulphur acquires an acid reaction in the air, by action of ozone, forming sulphuric acid.

274. **The Acids of Sulphur** here described for qualitative work are the following:

Hydrosulphuric	acid,	H_2S'',	forming	sulphides.
Sulphuric	"	$H_2S^{VI}O_4$,	"	sulphates.
Sulphurous	"	$H_2S^{IV}O_3$,	"	sulphites.
Thiosulphuric or Hyposulphurous	"	$H_2S''_2O_3$,	"	thiosulphates or hyposulphites.

Hydrosulphuric Acid.

275. Hydrosulphuric acid, H_2S, is a gas sparingly soluble in water, both the gas and the solution being in chemical use. **It is prepared** by acting on **ferrous sulphide** (one part) with **dilute sulphuric acid** (one and a half parts concentrated acid diluted to eight or ten parts)—(to saturate fifty parts of water with the gas). In open vessels the solution constantly loses gas; faster when boiled.

Ferrous Sulphide can be prepared by heating the middle of a bar of old iron to white heat, placing the bar over a tub of water, in a door-way or passage where the air-current is outward, and holding roll sulphur, by a pair of tongs, with the end of the roll upon the iron, as long as this is white hot. The iron sulphide granulates in the water. If the iron is only red hot, melted sulphur escapes combination and runs to waste.

The alkali and alkaline earth bases form super-sulphides. "Liver of sulphur" is K_2S_5, with lower sulphides. See, under Reagents, Ammonium Sulphide.

276. Most of the sulphides, those beside **As, Sb, Sn, Hg, Ag** (and **Pb**), are easily transposed by **dilute sulphuric acid,** the gas H_2S escaping with effervescence unless the solution is very dilute.

$$FeS + H_2SO_4 = FeSO_4 + H_2S$$

Hydrochloric acid, dilute, transposes sulphides of third group metals (except those of nickel and cobalt), not those of the second group (63).

The gas hydrosulphuric acid is recognized by its *odor,* and by blackening *lead paper*—white paper wet with lead acetate solution.

277. Nitric acid, unless very dilute, decomposes sulphides, at first with *separation of sulphur* (*a*), and, by continued action, dissolving the sulphur, which is oxidized to sulphuric acid (*b*):

$$a.\ 3CuS + 8HNO_3 = 3Cu(NO_3)_2 + 3S + 4H_2O + 2NO$$
$$b.\ 3CuS + 8HNO_3 = 3CuSO_4 + 4H_2O + 8NO$$

Mercuric sulphide is not changed by nitric acid—the separation of mercury in the systematic work of the second group.

278. The sulphides of the metals of the first three groups are insoluble in water (**Al** and **Cr** not forming sulphides), and *solutions of sulphides precipitate the metals of the first three groups*, as follows:

With **Zinc**	**salts**,	*zinc sulphide,*	white, sol. in dil. acid.
Ferrous	"	*ferrous sulphide,*	black, " "
Ferric	"	" "	" (with free S).
Aluminium	"	*alum. hydrate,*	(Equation, 77, note.)
Chromium	"	*chromium hydrate.*	
Manganese	"	*manganous sul.,*	flesh-color.
Copper	"	*cupric sulphide,*	black, insol. in. dil. ac.
Bismuth	"	*bismuthous sul.,*	black, " "
Lead	"	*lead sulphide,*	" " "
Silver	"	*silver sulphide,*	" " "
Mercury	"	*mercuric sulphide,*	(156) insol. in HNO_3.
Arsenic	"	*arsenious sul.,*	yel., sol. in $(NH_4)_2S$.
Antimonious	"	*antimonious sul.,*	orange " "
Antimonic	"	*antimonic sul.,*	" " "
Stannous	"	*stannous sulphide,*	brown, " "
Stannic	"	*stannic sulphide,*	yellow, " "

279. **Nitro-ferricyanides**, with soluble sulphides, or with hydrosulphuric acid after addition of an alkali hydrate, ammonium hydrate best, give an intense, rich *purple color*, slowly fading away. The test is best made on a white porcelain surface, using a few drops of each solution. Sodium nitroferricyanide, $Na_2FeNOCy_5$, is the reagent used.

280. Hydrosulphuric acid is a strong *reducing agent.* For reduction of ferric salts, see 99 *c;* the same by sulphides, 94; decoloring permanganate, 100; action on iodine, 221; on iodic acid, 232.

Sulphuric Acid.

281. The Sulphuric Acid of the pharmacopœia (sp. gr. 1.873), and that sold as chemically pure, are nearly absolute H_2SO_4, free from water. The old name "Oil of Vitriol" is

applied to any grade of the acid, but more often to impure acid, mixed with ten or fifteen per cent. of water. Sulphuric acid has a strong adhesive attraction for water, which it withdraws from the air, so as to dry the atmosphere in a desiccator, and the addition of water to the acid causes condensation of volume and elevation of temperature (see 22, Dilute Sulphuric Acid). Sulphuric acid chars organic bodies by taking from them the elements of water, leaving carbon.

All the common metals form normal sulphates, and potassium and sodium form acid sulphates, but the sulphates of bismuth, antimony, tin, and mercury are not very stable salts.

282. *Sulphuric acid transposes the salts of nearly all other acids,* except with chlorides and some other salts of mercury, silver, tin, and antimony. But at or near a red heat sulphates are decomposed by phosphoric acid; also by silicic acid.

283. Sulphuric acid, diluted, dissolves zinc and iron with effervescence of hydrogen (*a*). Concentrated sulphuric acid, heated, dissolves copper, mercury, silver, bismuth, and tin, with generation of sulphurous anhydride (*b*).

$$a.\ Fe + H_2SO_4 = FeSO_4 + 2H$$

$$b.\ Cu + 2H\,SO_4 = CuSO_4 + 2H_2O + SO_2$$

284. *Sulphates, and sulphuric acid, precipitate salts of lead, barium, strontium, and, if not very dilute, calcium.* The four precipitates are normal sulphates, and hydrochloric and nitric acids do not dissolve them, or do so but slightly and without transposition. Silver sulphate is only sparingly soluble in water, but most of the sulphates, besides the four above named, are freely soluble.

The test, and separation, of sulphuric acid are made, in most cases, by adding **barium chloride,** or barium nitrate, and treating the resulting precipitate with **hydrochloric acid** (or nitric acid): if the precipitate remains, it is evidence of sulphuric acid (unless hydrofluosilicic acid, or selenic acid, may be present).

285. Sulphates, *fused on charcoal with sodium carbonate*, give sodium sulphate (dissolved from the mass by water) and the other metal as carbonate, or oxide, or in metallic state (dissolved by dilute nitric acid). But some sulphide is formed (see, for Lead Sulphate, 145). If now, after long fusion on the charcoal, the mass is moistened and laid upon a silver coin, the presence of sulphide (reduced from sulphate) is shown by a black stain on the silver (Ag_2S). But it must first be made sure, by a blank test, that the charcoal and soda are free from sulphur. Ignition with sodium carbonate on porcelain does not reduce sulphates, and no silver stain is obtained (a distinction from sulphides).

Sulphurous Acid.

286. *Sulphurous anhydride*, SO_2, is a colorless gas with the strong stifling odor of burning sulphur. It bleaches litmus and other vegetable colors, and is a notable antiferment. It is dissolved by water, to the extent of about 14 per cent. of the cold solution, from which the gas constantly escapes unless it is kept in air-tight vessels. The solution probably contains *sulphurous acid*, H_2SO_3, (H_2O+SO_2). When sulphur is burned in the air (as in fumigating infected articles) it oxidizes wholly to sulphurous anhydride, SO_2; when it is treated with nitric acid or other oxidizing agent, it changes only to sulphuric acid, H_2SO_4.

287. *Solution of Sulphurous Acid* is prepared, U. S. P., by heating sulphuric acid with charcoal in a flask and conducting the gas, through a wash-bottle, into water: $2H_2SO_4 + C = 2H_2O + 2SO_2 + CO_2$. (Compare 283, *b*.) The carbon dioxide escapes, while the sulphur dioxide is dissolved. The solution first reddens litmus and then, if it be good, *bleaches* it. On standing it soon suffers oxidation into sulphuric acid, no longer bleaches litmus, and is odorless, and valueless as an antiseptic. So much of its precipitate with barium salt as refuses to dissolve with hydrochloric acid represents sulphuric acid (289).

288. On adding **almost any acid** to a sulphite, the latter is decomposed, and *sulphurous anhydride* gas, SO_2, arises rapidly, recognized by its odor, that of burning sulphur, as in ignition of ordinary matches, also by the bleaching of litmus-paper.

$$Na_2SO_3 + 2HC_2H_3O_2 = 2NaC_2H_3O_2 + H_2O + SO_2$$

289. *Sulphites precipitate the salts of non-alkaline metals,* only the alkali metal sulphites being readily soluble in water. The precipitates are soluble in dilute acetic, hydrochloric, and nitric acids. Free chlorine, bromine, strong nitric acid, and other *oxidizing agents* promptly change sulphites to sulphates.

Sulphites are identified, and separated from sulphates, as follows: to the solution **barium chloride** is added, and if a precipitate occurs **hydrochloric acid** is added. If a precipitate remains, it is filtered out (separation of *sulphate,* 284), and the filtrate is treated with **chlorine** (gas or solution). If a precipitate now appears it is sulphate formed from *sulphite* (290), and is evidence of the latter.

Ferric chloride, with sulphites, gives a red solution of ferric sulphite, or, in concentrated solutions, a yellowish precipitate of basic ferric sulphite, disappearing, decolored, on adding an acid.

290. *Sulphites are active reducing agents,* by virtue of their capacity for oxidation to sulphates:

$$H_2SO_3 + O = H_2SO_4$$
$$Na_2SO_3 + 2Cl + H_2O = Na_2SO_4 + 2HCl$$

By sulphurous acid, or its salts, ferric salts are reduced to ferrous (99 *d*), arsenic acid to arsenious acid, mercuric chloride (on boiling) to mercurous chloride, iodine is separated from iodic acid, and "colorless solutions of iodine" (see 221) are made.

Thiosulphuric (Hyposulphurous) Acid.

291. This acid, $H_2S_2O_3$, is hardly known, except by its salts, the thiosulphates. Hyposulphite of Sodium is extensively used in photography, and is used in medicine for effects very similar to the sulphite, as with dilute acids both alike form sulphurous anhydride (the potent antiseptic), thus:

$$a.\ Na_2S_2O_3 + 2HCl = 2NaCl + H_2O + SO_2 + S$$

$$b.\ Na_2SO_3 + 2HCl = 2NaCl + H_2O + SO_2$$

In the change stated in *a*, the excess of sulphur, distinguishing thiosulphate from sulphite, is set free. On the other hand, free sulphur will dissolve in sulphites, in certain conditions, forming thiosulphates.

292. *The addition of an acid*, then, gives fumes of *sulphurous anhydride*, SO_2, from thiosulphates as well as from sulphites (288), as shown in equation *a*, 291, but the *precipitation of sulphur* characterizes the thiosulphate.

293. The larger number of thiosulphates are **soluble** in water; the barium, lead, and silver thiosulphates being precipitated in solutions not too dilute, the silver precipitate soon blackening by reduction to sulphide. Calcium chloride does not precipitate thiosulphates (separation from sulphites).

294. Thiosulphates are *reducing agents*, stronger, even, than sulphites (hence their chief use in photography). They take iodine into combination instantly, forming iodide and a tetrathionate (*a*), so that sodium hyposulphite is often used to bleach iodine stains, is used in a fallacious "colorless solution of iodine," and is employed in volumetric estimation of iodine:

$$a.\ I + Na_2S_2O_3 = NaI + NaS_2O_3$$

With active oxidizing agents, in the dry way, as with chlorates or nitrates, hyposulphites form dangerous *explosive mixtures* (208).

295. PHOSPHORUS is a solid, easily fused and vaporized, and having several different physical states, or allotropic modifications. *White or ordinary phosphorus*, that of the U. S. P., crystallizable, is luminous in the dark, and in the air soon takes fire without being lighted, but it does not decompose water. It is poisonous. *Red or amorphous phosphorus* can be exposed to the atmosphere without change. It is not poisonous. Both these varieties are used in the manufacture of matches, with potassium chlorate or nitrate, or other oxidizing agents.

296. The Acids of Phosphorus, to be here given, are—

Phosphoric Acid,			
Orthophosphoric,	$H_3P^{v}O_4$,	forming	orthophosphates.
Pyrophosphoric,	$H_4P^{v}_2O_7$,	"	pyrophosphates.
Metaphosphoric,	$HP^{v}O_3$,	"	metaphosphates.
Hypophosphorous Acid,	$H_3P'O_2$,	"	hypophosphites.

Phosphoric Acid.

297. Orthophosphoric Acid, H_3PO_4, is a solid, feebly crystallizable, but so deliquescent as to be usually had in a syrupy consistence. It is not in commerce as a solid, but is U. S. Pharmacopœial in a 7.4 per cent. water solution, as "*Diluted Phosphoric Acid*," to be prepared either by oxidation of phosphorus with dilute nitric acid, or by hydration of Glacial Acid (HPO_3). Heat dehydrates orthophosphoric acid, first to pyrophosphoric acid, then to non-volatile metaphosphoric acid, but not to phosphoric anhydride. The last-named compound, P_2O_5, is a solid slowly volatile at white heat without chemical change.

298. Metaphosphoric Acid, HPO_3, is the "*Glacial Phos-*

phoric Acid" of the U. S. P. and of commerce. That sold, however, contains thirty to fifty per cent. of the sodium salt, $NaPO_3$, pure metaphosphoric acid being a waxy, viscid solid.

299. The leading phosphate in commerce is disodium hydrogen phosphate, crystallized, $Na_2HPO_4.12H_2O$, the common reagent solution; "Phosphate of Sodium," U. S. P. Bone Earth is about 90 per cent. of normal calcium phosphate, and is the most common source of phosphorus compounds. The "Phosphate of Iron," U.S.P., is ferrous hydrogen phosphate, $FeHPO$; the B. P. preparation of same name being normal ferrous phosphate, $Fe_3(PO_4)_2$. "Pyrophosphate of Iron," U. S. P., is ferric pyrophosphate, $Fe_4(P_2O_7)_3$, with ammonium citrate to render it soluble.

Phosphoric acid, tribasic, has three kinds of salts, two sorts of acid salts and the normal salts, thus:

Normal,	Na_3PO_4, trisodium phosphate;
	$Ca_3(PO_4)_2$, tricalcium diphosphate.
Two-thirds metallic,	Na_2HPO_4, disodium hydrogen phosphate
	$CaHPO_4$, calcium " "
One-third metallic,	NaH_2PO_4, sodium dihydrogen "
	$CaH_4(PO_4)_2$, calcium tetrahydrogen diphosphate.

300. The Orthophosphates, *normal and two-thirds metallic*, are insoluble in water, except those of the ordinary alkalies. But these insoluble phosphates, except those of lead, antimony, mercury, and tin, are dissolved by phosphoric acid, and by most other acids, through formation of acid phosphates only one-third metallic. *All non-alkaline bases, then, are precipitated by phosphates*—that is, by common sodium phosphate, Na_2HPO_4, and other alkali metal phosphates two-thirds metallic or normal. Precipitated phosphates, except ferric, aluminium, and lead phosphates, are mostly dissolved by **acetic acid.** Silver phosphate is pale yellow (pyrophosphate, white). For **Mg**, 57 *c*.

301. *Phosphoric acid can be separated from alkaline earth bases;* thus, in **$CaHPO_4$**, the acid radical can be separated from the calcium; by ferric salt and acetic acid, as follows: either dissolve in acetic acid, or dissolve in hydrochloric acid and add sodium (or potassium) acetate, then add, carefully, ferric chloride, not in excess. Ferric phosphate is precipitated, and calcium salt left in solution:

$$\mathbf{CaCl_2 + 2H\ PO_4 + 6NaC_2H_3O_2 + Fe_2Cl_6 = Fe_2(PO_4)_2 + 6NaCl + CaCl_2 + 6HC_2H_3O_2}$$

302. Any solution containing phosphoric acid and non-alkaline bases is precipitated by neutralizing it with any alkali. The solution obtained by dissolving calcium phosphate, or other alkaline earth phosphate, is *precipitated, as phosphate, in the third group of bases.* In this case, the phosphoric acid radical may be removed as directed in 301.

303. Ammonium molybdate, in its nitric acid solution (196), added to solutions containing phosphoric acid (or phosphate), gives a pale yellow precipitate, ammonium *phosphomolybdate*, forming slowly: **a delicate test.** The reagent must be in excess. For traces, set aside several hours.

304. Orthophosphoric acid, free, **H_3PO_4**, does not precipitate solution of ferric chloride (a distinction from both Pyrophosphoric acid and Metaphosphoric acid, also, from orthophosphates). Orthophosphoric acid, and Pyrophosphoric acid, likewise their salts with acetic acid, do not coagulate albumen or gelatine (distinction from Metaphosphoric acid).

At a dull red heat, disodium hydrogen phosphate is converted into pyrophosphate (the solution giving a white precipitate with silver nitrate). By the same means sodium dihydrogen phosphate is permanently converted into metaphosphate.

Hypophosphorous Acid.

305. Calcium hypophosphite is made by boiling phosphorus, with lime, in water, phosphorous hydride escaping, and taking fire in the air, as the bubbles rise.

$$3Ca(OH)_2 + 8P + 6H_2O = 3CaH_4(PO_2)_2 + 2PH_3$$

From this calcium salt, alkali hypophosphites are manufactured by transposing, in solution, with alkali carbonates.

The salts of hypophosphorous acid, $\mathbf{H_3PO_2}$, are acid salts, one-third metallic, as $\mathbf{NaH_2PO_2}$ and the calcium salt in the equation, above.

306. The hypophosphites are all **soluble in water,** and give no precipitates by transposition.

They are, however, so strong reducing agents that they precipitate silver, mercury, and other salts, by reduction. With **mercuric chloride,** first a white precipitate of *mercurous chloride*, then a gray one of *free mercury*, is obtained.

On ignition, hypophosphites decompose, with explosive burning of the phosphorous hydride formed, while pyrophosphate is left:

$$2CaH_4(PO_2)_2 = Ca_2P_2O_7 + H_2O + 2PH_3$$

The distinctive odor of $\mathbf{PH_3}$, and its deflagration, make this a characteristic reaction. With all oxidizing agents, as chlorates, nitrates, permanganates, etc., in dry mixture, hypophosphites are *violently explosive!*

Boric or Boracic Acid.

307. Orthoboric acid, $\mathbf{H_3B'''O_3}$, and metaboric acid, $\mathbf{HB'''O_2}$, are the chief acids of boron; by their ignition, boric anhydride, $\mathbf{B'''_2O_3}$, is obtained in a vitreous state. The compound of boron having commercial importance is sodium superborate (diborate), $\mathbf{(NaBO_2)_2B_2O_3}$, or $\mathbf{Na_2B_4O_7}$, crystallized with $\mathbf{10H_2O}$, as common *Borax*, "Biborate of Sodium" U. S. P.

308. The non-alkali borates are insoluble in water, and, hence, *alkali metal borates in solution precipitate salts of most non-alkali bases.* With **silver nitrate**, sodium diborate gives a white precipitate of *silver borate;* normal borates, a brown precipitate of silver oxide. With **lead** salts, and with **barium** and **calcium** solutions not too dilute, white precipitates of normal borates are obtained; with **aluminium** salts, aluminium hydrate.

309. All ordinary acids—and in some conditions even carbonic acid—transpose borates, with formation of boric acid.

A characteristic test is by adding, in an evaporating dish, a little sulphuric acid, then adding **alcohol** (which dissolves boric acid), and lighting the alcohol. *A green flame,* most distinct at the lower border of the flame, indicates boric acid.

310. If a powdered borate, previously calcined, is moistened with sulphuric acid and heated on the loop of platinum wire to expel the acid, then moistened with **glycerine** and burned, the green flame appears very distinctly (**Iles**).

Borates, in the inner blow-pipe flame, give the green color to the outer flame.

Silicic Acid.

311. Silica is silicic anhydride, $Si^{IV}O_2$. It is nearly pure in rock-crystal, and is the substance of Quartz, Agate, Chalcedony, and Flint, the chief part of sand, and enters into the composition of a great number of minerals. Glass consists of silicates of potassium, sodium, lead, and other bases; Porcelain is made up principally of alumina and silica; and Soluble Glass, or water glass, is a soluble silicate of sodium or potassium.

Silicic anhydride combines with water to form several silicic acids, H_4SiO_4, H_2SiO_3, and others. These acids appear as "gelatinous silica," soluble in dilute acids. By a dry heat of 100° C. (212° F.), silicic acids leave the anhydride, SiO_2, insoluble in water and acids.

312. The soluble potassium and sodium silicates are formed (1) by long fusion of silica or silicates with three or four parts of potassium and sodium carbonates, in a porcelain crucible. The carbonates of potassium and sodium mixed in about molecular proportions melt easier than either alone. (2) Boiling with solution of potassium or sodium hydrate (in a bright iron or silver dish) dissolves silica, and decomposes many silicates, forming the alkali metal silicates.

If, now, the alkaline mass, fused as above, or the alkaline solution just mentioned, be treated with hydrochloric acid, in excess (that is, to acid reaction), the silicic acid, H_4SiO_4, is obtained free and dissolved. The bases of the original silicates will, in most cases, also dissolve, as chlorides.

In the test for silica, this acid solution (filtered clear, if need be) is evaporated and well dried at 100° C. (212° F.) The dried mass is treated with hydrochloric acid. A residue, not dissolved by hydrochloric acid, and gritty under the glass rod, is silica.

313. FLUORINE cannot well be preserved free, as it combines with the materials of vessels, except fluor-spar, and on contact with water forms *hydrofluoric acid*, HF. This acid is also prepared by transposing calcium fluoride (fluor-spar) with sulphuric acid. If silica be present, in this reaction, *silicon fluoride*, SiF_4, is formed. On passing silicon fluoride into water, *hydrofluosilicic acid* is obtained, $(HF)_2SiF_4$ or H_2SiF_6.

314. Hydrofluoric Acid, HF, is colorless gas, soluble in water. The solution is kept in gutta-percha bottles; it quickly corrodes glass, porcelain, and the metals except gold and platinum, and lead in a slight degree. Both the solution and its vapor act on the flesh as an insidious caustic, causing obstinate ulcers.

315. Calcium fluoride, Fluor-Spar or Fluorite, is the source of fluorine compounds. *The etching of glass* by hydrofluoric acid is done as follows: The glass is thinly and perfectly coated with wax, spread when melted, and the writing or lining is done through the wax coat. A paste of coarsely-powdered fluor-spar and concentrated sulphuric acid is now spread over the surface to be etched (avoiding contact of the vapor with the skin) and the article set aside for several hours.

A test for fluorides is made as above, or by adding concentrated sulphuric acid to the material in a little lead dish, made by bending sheet lead, and covering it for some time with a piece of glass coated with wax and marked through the wax.

316. Hydrofluosilicic Acid, H_2SiF_6, formed as stated in 313, is sometimes used as a precipitant for barium. Its salts of barium, sodium, and potassium are nearly insoluble in water, quite insoluble if alcohol be added. Most of the other silicofluorides are soluble in water.

317. Examination for Vaporous Acids.

Test I. *To a little of the solid substance, or residue by evaporation, or concentrated solution, in a test-tube, add a little* **Sulphuric Acid,** *and (if there is no effervescence) heat gently.*	**Result 1. There is Sudden Effervescence** (the vapor feebly reddens litmus) : **CO_2**, *from Carbonates.* Gas is colorless and odorless, and makes **calcium hydrate** solution turbid (261). Carbonates are not found in solutions holding non-alkali bases. Solutions of carbonates precipitate all bases but those of alkalies. *Oxalates*, with concentrated sulphuric acid, not with Acetic acid, slowly evolve **CO_2**. **Result 2. There is a gas having odor** (litmus-paper is reddened, or bleached) : **H_2S**, *from Sulphides.* Gas blackens paper wet with **lead acetate.** The sulphides, with hydrochloric acid, also, give **H_2S**, but with nitric acid or chlorine they separate sulphur, finally forming **H_2SO_4** (277). Sulphides precipitate the bases of the first three groups (278). **SO_2**, *from Sulphites.* Odor of burning sulphur. Litmus-paper is bleached (288). Gas colors **iodic acid and starch** (232). Sulphites precipitate all bases but those of alkalies (289). **SO_2**, *from Thiosulphates.* Gas as last above. Sulphur is precipitated (292). **Calcium salts** not precipitated by thiosulphates (293). **HCy**, *from Cyanides.* Peach-blossom odor. Gas precipitates **silver nitrate** solution on a glass rod (249). Changed to *sulphocyanate* (250),

gives blood-red color with ferric salts (251). **HCy,** *from Ferrocyanides,* 249.

$HC_2H_3O_2$, *from Acetates.* Vinegar odor. *Acetic ether* test, 271. **Ferric salts,** red solution (272). No precipitates.

HCl, *from Chlorides.* Slight effervescence. Slight, irritating odor. Gas precipitates **silver nitrate** solution, on a glass rod; the precipitate not dissolving in nitric acid (204, *a*). Chlorides precipitate salts of First Group Bases (205).

Result 3. There is a gas having Color: (Litmus-paper in most cases reddened.)

HI and I, *from Iodides.* Odor disagreeable and chlorine-like. Vapor turns violet, in the air, from separation of iodine. Test made better with **chlorine** water, and made as well in dilute solutions; **starch,** blue; **carbon disulphide,** violet (225). First Group Metals and **Hg''** precipitated by iodides (227).

HBr, *from Bromides.* Odor is acrid and chlorine-like. Color, if seen at all, is slightly yellowish-brown, from free bromine. Test made better by **chlorine** water, in solution not too dilute; **carbon disulphide,** yellow; **starch,** yellow (217). *If iodine is present,* it must be removed or oxidized, to find bromine (218). First Group Bases precipitated (219).

NO, *nitric oxide, from Nitrites, and sufficient quantity of solid Nitrates:* Color, brownish-red. Odor, characteristic. See 243. As to Nitrates, see below.

Cl *and Chlorine Oxides, from Chlorates.* Color greenish-yellow. *Crackling or explosion.* Litmus bleached. No precipitates. See 209.

Cl, *from Hypochlorites.* Original material bleaches litmus. See 212.

Result 4. There is no appearance of the generation of a gas:

HNO_3, *from Nitrates.* See NO, etc., above. The "*brown ring test,*" (238, *a*). No precipitates (241).

HF, *from Fluorides.* Etching test (315).

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318. Examination for certain Non-Volatile Acids.

For Silicic Acid: Fusion with alkali, acidulation, evaporation and drying, acidulated water (312).

For Boric Acid: Flame tests (309).

For Hydroferrocyanic Acid: In a solution, test by 254. If insoluble in water, digest with potassium hydrate, filter, and test filtrate.

For Hydroferricyanic Acid: Solution test by 256 (iron salts). If not soluble in water, treat with potassium hydrate, as above, and test filtrate.

For Sulphocyanic Acid: Test by 257 (Ferric salts).

319. For Sulphuric, Oxalic, and Phosphoric Acids, in Solutions.

If the solution is acid to test-paper, make it nearly or quite neutral, by adding ammonium hydrate, but not to the extent of causing a precipitate.

Add **Barium** *and* **Calcium Chloride.*** **Precipitate: $BaSO_4$, CaC_2O_4, phosphates.†**

If there is a precipitate, *add* **hydrochloric acid,** and leave a few minutes.

Remaining Precip. $BaSO_4$. See 284.

Sulphates precipitate salts of Pb, Ba, Sr, Ca.

Solution: $H_2C_2O_4$, H_3PO_4 or $CaH_4(PO_4)_2$; barium and calcium chlorides.

Add **Ammonium hydrate,** *to a slight alkaline reaction.*

Precipitate: CaC_2O_4, $CaHPO_4$. (*If there is much liquid decant from it.*)

Add to the precipitate, **acetic acid** *to a sharp acid reaction.*

Remain'g Precip. CaC_2O_4.

Further, for Oxalates, see 266.

Solution: $CaH_4(PO_4)_2$ (300).

Add **ammonium hydrate** *to alkaline reaction.*

Precipitate: $CaHPO_4$.

Test the dissolved Pre., or the original solution, with **Molybdate** (303).

With **Ferric chloride** and **Acetate** (301).

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* If the solution contains First Group Bases, these must be removed, by full precipitation with H_2S and filtering.

† Precipitates of other acids may be here obtained—viz., borates, silicates, fluorides, sulphites, chromates, arseniates, iodates, ferrocyanides, tartrates, citrates.

320. Tests by the Blow-pipe, with Borax, on Platinum Wire.

The loop of platinum wire, red hot, is dipped in the powdered borax, which is then fused to a clear bead. The hot bead is brought in contact with the substance (in powder), and fused again until clear, first in the outer or oxidizing flame, then in the inner or reducing flame.

In the table, *h* signifies the hot bead; *c*, cold bead; *sups.*, supersaturated with the substance tested; *s.s.*, strongly saturated.

Color of the Bead.	**In outer, or oxidizing Flame.**	**In inner, or reducing Flame.**
Yellow or Brownish.	*h.*, *not sat.* Iron.	*h.* Molybdenum.
Red.	*h.* Iron. *c.* Nickel.	*c.* Copper (*sups.*, *opaque*).
Violet or Amethyst.	Manganese. *h.* (Nickel with Cobalt.)	
Blue.	*h.* and *c.* Cobalt. *c.* Copper.	*h.* and *c.* Cobalt.
Green.	*c.* Chromium. *h.* Copper. (Iron with Cobalt or Copper.)	Chromium. *sups.* Iron.

CONVERSION OF SOLIDS INTO LIQUIDS.

321. Before the fluid reagents can be applied, solids must be reduced to liquids. To obtain a complete solution the following steps must be observed:

First. The solid, reduced to a fine powder, is boiled in ten times its quantity of **water.** Should a residue (*a*) remain, it is allowed to subside, and the clear liquid poured off or separated by filtration. A *drop* or *two*, evaporated on glass, or clean and bright platinum foil, will give a residue, if any portion has dissolved. Also, the solution may be tested for the metals of the groups. If a solution is obtained, the residue (*a*), if any, is exhausted and well washed with hot water.

Second. The residue (*a*), insoluble in water, is digested some time with hot **hydrochloric acid.** The residue (*b*), if any remains, is separated by filtration and washed, first with a little of this acid, then with water. The solution, with the washings, is reserved.

Third. The well-washed residue (*b*) is next digested with hot **nitric acid.** (Observe if there are any vapors of nitrogen oxides, indicating that a metal or other body is being oxidized, also if sulphur separates, 277 *a.*) If any residue (*c*) remains it is separated by filtration and washing, first with a little acid, then with water, and the solution reserved.

Fourth. Should a residue (*c*) remain, it is to be digested with **nitro-hydrochloric acid,** as directed for the other solvents. If this does not dissolve it all, the residue (*d*) is treated according to *Fifth.*

The acid solutions are to be evaporated nearly to dryness and then redissolved in water, acidulating, if necessary, to keep the substance in solution.

Fifth. Should the substance under examination prove insoluble in acids, it is likely to be either a sulphate (of barium, strontium, or lead), a chloride or bromide (of silver or lead), a silicate, or fluoride; and it ***must be fused with a fixed alkaline carbonate,*** when the constituents are transposed in such a manner as to render them soluble. The water solution of the fused mass will be found to contain the acid; the residue, insoluble in water, will contain the base, now soluble in hydrochloric or nitric acid (compare 145).

If more than one solution be obtained, by the several trials with solvents, the material contains more than one compound, and the solutions (*First, Second, Third,* etc.,), as separated by filtration, should be preserved separately, as above directed, and analyzed separately. The separate results, in many cases, indicate the original combination of each metal.

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[From the *Chemical News* (London), June 15, 1877; xxxv., 251.]

This book ["DOUGLAS AND PRESCOTT'S QUALITATIVE CHEMICAL ANALYSIS"] is in reality, as its second title affirms, a guide in the practical study of chemistry and in the work of analysis. It is not a mere body of directions to be blindly followed by the student without his having learnt the reason why. If this book be faithfully studied, the habits of "automatic operation" and "superficial observation"—too often the only acquirements learnt in a laboratory—will be accompanied by a sound knowledge of the *principles* on which the plans of qualitative analysis are based. Indeed, if we had before us for review nothing but one more mere manual of analysis, distinguished from the ever-increasing crowd of such manuals, to which the attention of teachers and learners is being continually called, by no distinctive superiority, we doubt whether our readers would have thanked us for noticing the book. But the volume before us shows so many marks of ability in its conception, and care in its execution, that it is a real pleasure to speak decisively in its favor.

In criticising a volume on chemical analysis, the minuter details of the treatment adopted would be out of place. But we may give our readers a summary of the contents of the book, and we may also convey some notion of the style in which the subject is handled in a very few lines.

After a few preliminary remarks, very sound and intelligible, on the study of chemical analysis, we reach the two chief chapters of the book, relating to the reactions of the metals and acids, respectively. Here the rarer metals and non-metals are introduced, but the rarer organic acids are excluded as not admitting of adequate discussion in a manual for students' use. Indeed, if we include such organic acids as succinic and salicylic in a handbook of ordinary qualitative analysis, such organic bases as methylamine and quinine can scarcely be omitted. Nearly two hundred pages are thus occupied with what may be called the *comparative* chemistry of the metals and bases of the non-metals and acids. There is no shirking of explanations. Reactions are duly displayed, while a running commentary explains at once why certain properties and changes are utilized in the processes of separation, and, also, how this is done. That the reactions are chronicled with adequate fulness may be gathered from a single example which we take, haphazard, from the account of iron compounds, which occupies more than five pages (47 to 52):

"Iron dissolves in hydrochloric acid and in dilute sulphuric acid, to ferrous salts, with liberation of hydrogen (*a*); in moderately dilute nitric acid, with heat, to ferric nitrate, liberating chiefly nitric oxide (*b*); in cold dilute nitric acid, forming ferrous nitrate with production of ammonium nitrate (*c*), of nitrous oxide (*d*), or of hydrogen (*e*):

a. $Fe + H_2SO_4 = FeSO_4 + 2H$.

b. $2Fe + 8HNO_3 = Fe_2(NO_3)_6 + 2NO + 4H_2O$.

c. $4Fe + 10HNO_3 = 4Fe(NO_3)_2 + NH_4NO_3 + 3H_2O$.

d. $4Fe + 10HNO_3 = 4Fe(NO_3)_2 + N_2O + 5H_2O$.

e. $Fe + 2HNO_3 = Fe(NO_3)_2 + 2H$."

After the foregoing reactions and plans of separation, we find a concise account of the "Preliminary Examination," including blow-pipe analysis; then follows the systematic analysis of solutions, and a full account of the solubilities of salts. The two pages (245–6) devoted to Reagents do not suffice for a useful discussion of this subject.

[From the *American Journal of Pharmacy* (Philadelphia), May, 1875; xlvii., 236.]

A work like this ["PRESCOTT'S PROXIMATE ORGANIC ANALYSIS"] has been needed for a long time, and although it does not cover as much ground as we should have desired for it, yet it is a very valuable addition to our literature, and will prove of great service to those engaged in proximate analysis, since there is not, to our knowledge, another work in the English language in which the same kind of information is given in such a comprehensive and conveniently-arranged style. The author himself states that "this compilation is fragmentary and very brief," and we have, therefore, no reason to find fault with the absence of such compounds as gentiopicrin, arbutin, etc., or with the brevity with which a number of the alkaloids and neutral principles have been treated.

[From the *Chemical News* (London), July 23, 1875.]

Proximate organic analysis may be described as a comparatively untrodden field. The best authorities at our disposal do little more than give us the directions for detecting, isolating, and determining a few of the best-known organic acids and bases. . . . Under these circumstances, we naturally welcome every chemist who attempts to supply so important a desideratum. Mr. Prescott arranges the substances of which he treats as solid fixed acids; solid volatile acids; liquid fixed acids; liquid volatile acids; fatty acids, liquid and solid; neutral substances; bases; glucosides; nitrogenous neutral bodies; carbohydrates, and alcohols. . . . We trust that he [Mr. Prescott] will find ample opportunity to continue the important undertaking upon which he has entered.

[From the *Journal of Applied Chemistry*, Jan., 1875.]

The first and only book published in the English language which attempts to give in a concise form the reactions of organic substances. . . . A great service to the analyst.

[From the *Mining Journal* (London), March 20, 1875.]

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[From the *Quarterly Journal of Science*, London.]

We may finally characterize this work ["PRESCOTT'S CHEMICAL EXAMINATION OF ALCOHOLIC LIQUORS"] as a valuable complement to the labors of Mr. Allen, Professor Wanklyn, and others of the much-abused public analysts who are successfully striving to place the chemical examination of food upon a sound and sure basis.

[From the New York *Tribune*, March 5, 1875.]

It abounds in details of great interest for popular use, no less than in a scientific point of view, comprising much valuable knowledge in a small compass.

[From the *Chemical News* (London), Sept. 24, 1875.]

The author gives, in a terse, compact form, a great amount of information on alcoholic beverages—their normal constituents, their impurities, and the intentional sophistications to which they are liable. . . . This little volume will prove highly useful to the public analysts.

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